

PROFIT OPPORTUNITIES  
FOR THE  
CHEMICAL PROCESS INDUSTRIES

Joint  
National Aeronautics and Space Administration  
and Battelle-Columbus  
Seminar

Columbus, Ohio  
November 16, 1971

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Prepared by  
BATTELLE  
Columbus Laboratories  
505 King Avenue  
Columbus, Ohio 43201

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NASA/Battelle-Columbus  
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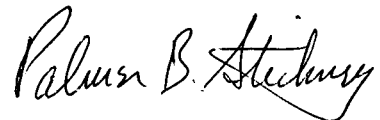
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## FOREWORD

These Proceedings cover a Technology Transfer Seminar held as part of a continuing effort by NASA to assist industry in the utilization of NASA-developed technical innovations. The Seminar was held at Battelle's Columbus Laboratories in Columbus, Ohio, on November 16, 1971.

The program was arranged primarily for representatives of the chemical industry. Some of the topics included were chosen to demonstrate the processes by which some developments were already being commercialized. In addition, others were selected to suggest some areas in which NASA technology was available that could be useful to the chemical industry. There are, of course, many more areas of technological development in which there are NASA-sponsored developments that could be of great value to the chemical industry. In one of the early general talks on the program, Dr. James Burnett of NASA described the Technology Utilization program of NASA rather completely. It is recommended that the reader refer to this talk as a guide to procedures for obtaining more information regarding NASA developments in any technological area.



Palmer B. Stickney  
Seminar Chairman

Approved by  
Mr. Leonard A. Ault, Chief  
Program Control and Support Division  
Technology Utilization Office  
National Aeronautics and  
Space Administration  
Washington, D. C. 20546

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## INTRODUCTION AND WELCOME

Roger L. Merrill  
Director, Battelle, Columbus Laboratories

Gentlemen, it is a special pleasure for me to welcome you here today. As you may know if you have had an opportunity to peruse some of Battelle's literature out in the lobby, Battelle's stated purpose or reason for being, if you will, is the advancement and utilization of science for the benefit of mankind through the processes of technological innovation. It is for this purpose that we have been working with NASA's Office of Technology Utilization for a number of years. Our efforts have been directed mainly toward making NASA technology available and of benefit to industry and the public sector. This seminar today is something of an experiment. It is one more effort to bring about the stated goal and we hope that it will be a useful tool for that purpose because it does so closely fit NASA's and our own reason for being. I do not think it would be appropriate for me today to take time from your schedule to talk about the glories of Battelle. Let me say that it is a pleasure for me to welcome you here and we hope that you will have a very profitable day. If there is anything that we can do to make it more profitable and more useful to you, please do not hesitate to call on us. Thank you very much and have a good day!

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## NASA'S TECHNOLOGY UTILIZATION PROGRAM

J. E. Burnett

NASA Lewis Research Center, Cleveland, Ohio

The first NASA satellite was Explorer 1. It was in orbit for about 12 years, weighted a total of 31 pounds and decayed in the Spring of last year. Today we have the capability of putting into orbit a satellite that weighs about 300,000 pounds. This past decade has also seen the first man on the moon and the advent of communication and weather satellites. These are now a part of the total fabric of our society.

To accomplish these things and others like them, NASA has had to conduct basic research, applied research, development, and experimentation and test in an extraordinarily wide range of scientific disciplines and technical fields: chemistry, metallurgy, electronics, basic materials sciences, mathematics, computers, combustion, fabrication, bearings, lubrication, rotating machinery, management systems and so on and on. The list is not endless, but it is very long indeed. The scientific and technical efforts in these many fields have produced a tremendous outflow of aerospace-related new technology. The NASA Technology Utilization (T.U.) Program was established about 8 years ago in order to speed the transfer of this aerospace-related new technology to the nonaerospace community.

A fair question, I suspect, would be: why such a program? Why exert any special effort to transfer this technology? The answer to that, of course, is easily given. It just requires that we remind ourselves of something that we all know very well indeed -- industry is based on technology applied to products and the methods of manufacture and distribution, and continued profitable growth depends greatly on new technology applied to product and production improvements, new developments, and complete new enterprises. That, of course, is hardly news to this group. Your chemical processing industry is one of the more spectacular examples of technology-related change and growth, and so, the NASA TU Program seeks to transfer aerospace-related new technology to industry and commerce for their creative application. And let me stress the creative application, because seldom will we transfer technology which can be used immediately in its existing package. More often we transfer a technological base which you can use as a point of creative departure.

There is involved here, of course, in this effort to transfer aerospace technology an unspoken but essential premise, the premise that the technology is worth transferring. That is, the premise that aerospace technology does have a substantial content of value for nonaerospace uses. We could spend this morning, were we so inclined, looking at a long list of transfers, items that show aerospace technology being used for nonaerospace purposes. With this particular group, that is not necessary. Instead, I would like to look briefly at a communication experiment conducted by the Lewis Research Center of NASA. The experiment was conducted to test this particular premise of the value of aerospace technology for nonaerospace uses. As a part of the TU program at Lewis we conducted this experiment with the petroleum industry. We picked petroleum essentially because of its sophisticated technical and communications skills.

Having decided on a communication experiment we contacted ESSO Research and Engineering, a division of Standard Oil of New Jersey. We set forth two specific objectives. We said we would like to work with them first to find areas of common interest. (We suspected that this would not be too hard, since there were some pretty obvious ones such as bearings and lubrication and we also suspected that there might be other much more subtle areas of common interest.) The second objective, was the important one; the second objective was to reduce the areas of common interest down to just those, where in ESSO's judgment the technology was of real use and value to their industry and was new to them.

We had some ground rules. First, there would be no government contract involved. We were not interested in a contractor relationship. We wanted the attention and thought of people whose time we could not buy. Also, we wanted any benefits to come from positive results of the experiment, not from a fee-paying government contract. The second ground rule was that the results of the experiment were to be communicated to all parts of the petroleum industry, which made this a public service effort on the part of ESSO. The third, sort of obvious, ground rule was that there would be no classified information from our part and no proprietary information from ESSO's part.

We put together composite teams formed of senior technical people from petroleum and senior technical people from aerospace. Over a period of about 9 months we had meetings, exchanged reports, telephone calls, and letters, and met again for technical dialogue--all in the examination of aerospace technology to meet these two objectives. The search results were very highly positive. That is, new technology which met these criteria of being new to ESSO and which was in their judgment of real value to the petroleum industry was identified again and again and again. It was not in bits and pieces; it was in very large packages; and it was far from being trivial. It occurred in some very obvious areas like lubrication, but it also occurred in such areas as combustion and heat transfer, and in such relatively esoteric and unexpected areas as surface physics and chemistry. (We have been conducting research on what happens to a spacecraft surface when it is exposed to high vacuum and hard radiation in space. The information we were deriving turned out to be of interest to petroleum because of its catalyst-related nature.)

And so in company with ESSO we went to the American Petroleum Institute. We told them what we had been about and the results thereof, and suggested that an industry conference might be useful. We asked for their comments. The Institute conducted a market survey. They contacted the 20 largest petroleum producers, reported to them what had happened and asked for their comments regarding a conference. All 20 companies responded and the answers were highly favorable. Accordingly, we held a conference.

For 2 days we briefed technical managers and executives from the petroleum industry. We briefed them on what ESSO had come up with. The presentation was put on by technical panels from Lewis Research Center. Just one more conference, I suppose, in a way, except the results were interesting and conclusive. We received the usual commendatory telephone calls and letters, of course. More important, we received calls requesting more information, and we received calls requesting private conferences. We entered into a substantial technology dialogue with the petroleum industry.

Interestingly, the number of petroleum companies directly working with NASA in this TU program went from three or four before the conference to about fifteen within 2 or 3 months after the conference. We are still in regular, though intermittent, dialogue with companies like Ashland Oil. The petroleum industry seems now to have made aerospace technology a working part of their total corporate technological resources.

Petroleum is a sophisticated, technology-based industry, and the results of our experiment would seem to be clear proof of our original premise. Aerospace-related technology does have a substantial content of value for non-aerospace uses. We have further verified this premise, incidentally, by similar work with the electric power generation industry. I can assure you, indeed almost guarantee you, that your efforts to enter into a regular examination of aerospace technology will prove to be very much worth your time and cost.

Let us now briefly examine the NASA TU program. We have a highly active, not a passive program, for we are decidedly not inclined to believe that a passive program really does much to transfer technology.

First, there is a NASA TU officer at each NASA Field Center. This man, together with the technical staff assigned to him, is charged with a variety of duties. First he retrieves in-house technology. All of the NASA Field Centers are major research and development institutions with a substantial in-house capability. Secondly, he retrieves technology from our contractors. Thirdly, he and his staff evaluate this technology for its potential significance, non-aerospace "merit" for dissemination. And lastly, they help to disseminate the selected technology. Perhaps most important of all, in their dissemination, they form a working interface with industry and commerce. At any time that you have an interest in exploring NASA technology, one of the most productive first things to do is to get in touch with the TU officer at the NASA Field Center nearest to you. That will start the process, and there is no obligation and no charge.

Under the TU program we produce a variety of special publications. Many have demonstrated a very high utility to American industry. First of these NASA TU publications is the Tech Brief. These are a single-page document which report on particular innovations that have come from NASA research, either in-house or under contract. Over 4,000 Tech Briefs are now in existence and cover innovations of a very wide variety.

The second kind of TU publications is compilations. These are short booklets which include a group of related innovations. A compilation of innovations on the Synthesis of Fluorinated Hydrocarbons is an example. Technology Reports and Technology Surveys issued by TU are more substantial documents. They survey NASA contributions to the advance of the art in science and technology in specific fields. An example here is the Survey on Analytical Chemistry Instrumentation.

Lastly, we produce Conference Proceedings. The proceedings of the Conference on Selected Technology for the Petroleum Industry is a representative TU publication. Over the years since the conference was held, several thousand copies have been sold.

We can furnish you a listing of TU publications for your review.



Perhaps the most active part of the NASA TU program in the sense of the interface with industry lies in our dissemination efforts. This conference at Battelle is one example. Also, we have a number of Regional Dissemination Centers. These are university-based centers for the transfer of technology to industry, and I will talk a little bit more about those in just a minute. We have Bio-Medical Application Teams (BATEams), located at various research institutes. In this BATEam program TU supported teams of scientists interface with medical research institutions with the basic question: What is impeding your medical research? They then convert the answer into physical science and technology terms which we use to search the massive NASA data bank. A number of technology transfers have resulted from this particular program; transfers like X-ray enhancement where the technique of computer enhancement of telemetered lunar pictures is now being applied to medical X-rays.

We have Technology Application Teams which, like the Bio-Medical Teams, are charged with the transfer of technology with respect to specific problems. The difference is that these Technology Application Teams work in the public sector. Some public sector applications work is also conducted by NASA Field Centers. Lewis, my particular Center, has, for example, worked very closely with organizations like the Cleveland Clinic in medical research and with the City of Cleveland in connection with a clean-water program.

Continuing this brief look at technology transfer and special dissemination programs, it is noted that we have interagency agreements with other government agencies like NIH, the Department of Transportation, the Environmental Protection Administration, the National Science Foundation, HEW, etc., calling for the examination or application of aerospace technology to a variety of needs.

Let us consider further the NASA Regional Dissemination Centers (RDC) for these form a basic communication link. Regional Dissemination Centers provide a mechanism for the regular, continuing, working access to aerospace technology.

These RDC's are located at Indiana University, The University of Pittsburgh, ~~Pittsburgh~~, University of Connecticut, University of Southern California, the University of New Mexico, and the North Carolina Science and Technology Research Center. A special RDC for the dissemination of computer programs is at the University of Georgia.

NASA puts in two things into these RDC's. We put in money to start the RDC and we put in the NASA data bank. The NASA data bank comprises today about 700,000 documents and is being added to at the rate of about 7,000 documents per month. It results from the NASA world-wide literature collection effort. The NASA data bank contains documents from many sources -- about one-fourth NASA and its contractors, one-fourth DOD and its contractors, one-fourth other domestic sources, and one-fourth foreign sources (Europe, Russia, and so on).

NASA started this data bank as a resource for use in conducting its main missions in R&D and space flight, but through the TU program it is now available to American industry. The data bank is under full bibliographic control, that is, it is indexed, it is multiple cross-indexed, and, most important, it is indexed on magnetic tape for computer search and retrieval.

The RDC then provides to each fee-paying industrial customer a mix of computer-based search and retrieval and personal services. All of these RDC's started with the NASA data bank as their fundamental data resource. Because the program has been successful, these data bank resources have now been expanded, and we find that the RDC's offer to their industrial customers not only the NASA data bank but those from other government agencies like AEC, together with a large number of private files, as, for example, the Engineering Index, the Chemical Abstracts Condensates and the Index Medicus. Their data resources have become quite large.

The fees at the RDC's range from about \$200 for a one-subject search for a small business up to the larger customers who are paying several thousand dollars a year. The industrial membership lists of these RDC's read like a bluebook of American industry.

Although RDC services are by no means a "final" answer to the technical information problem, they offer to industry a highly valuable resource. It is obvious that computer search and retrieval does not replace the creative insights of the human mind. It has long since become impossible, however, for the individual to personally search any substantial fraction of the world's annual technical output. Computer search and retrieval of technical information will necessarily become an everyday part of industrial technical practice. RDC membership offers you a chance to learn how to make mechanized retrieval work for your company.

Let me close with an invitation. If you are interested in aerospace-related technology and want more information on the NASA TU program, just write or call me -- or the TU Office at NASA Headquarters or any NASA Field Center.

## THE GENESIS OF THIS SEMINAR

H. R. Batchelder  
Battelle, Columbus Laboratories

I want to address myself particularly to this specific seminar.

You have heard that we have been involved in the technology utilization program for a number of years. The wide spread of Battelle's scientific and technical capabilities and the years of close association with Government and industry have put us in a unique position to further the application of NASA technology to nonaerospace uses.

Mr. Burnett has told you that NASA had made efforts along many lines to make the results of their remarkable work of more utility to the industrial and public sectors. He has told you about the wide range of publications, other industry-oriented seminars, films, exhibits, the services of the Regional Dissemination Centers, and many others. Considerable success has been achieved in transferring the NASA technology and many significant benefits have resulted. Only a small part of these benefits is directly visible; NASA's indirect contributions have been very extensive.

One obstacle that is almost always present is the fact that the NASA technological advances are rarely in a form to be applied directly to industry. More study has to be done, more work performed, and in many cases new inventions made before an industrial firm can capitalize on the work that NASA has done. We at Battelle have been conscious of this and frustrated by it for quite some time, but had not seen yet any easy way to overcome it.

A second barrier to effective transfer has been the patent situation. As you all know, the risk of transferring any new technical development from laboratory or pilot plant to production line is the largest risk in the whole development chain, and rarely is it undertaken without some assurance of a proprietary position or protection over the long term.

It occurred to us that we might select a few examples of NASA innovations that seemed to have potential for further development, look at the ways the original idea could be expanded, modified, or extrapolated, and at the work that would have to be done to make commercial production economically attractive.

We felt quite strongly that there were many NASA innovations that were suitable as starting points for research--ideas that might not be directly suitable for commercial exploitation, but might hold significant promise if modified or enlarged. Further, many of NASA's needs were satisfied with the production of one or only a few items with cost not the significant factor. In order to succeed at commercial production, it probably would be necessary to do a considerable amount of work on manufacturing methods, cost reduction, alternative raw materials, and the like.

If this were the case, any inventions made in the course of these research programs if privately supported, could be privately patented, and

the necessary long-term protection provided in this way. To reinforce this, there have been some changes in the NASA patent policy that make exclusive licenses possible under some conditions. This will be discussed in a little while.

The purpose of this seminar, then, is to present a possible approach to the use of NASA innovations. To do this, we have selected four examples--and I would like to emphasize that they are only examples to illustrate the methods--not nuggets of gold waiting to be picked up.

For each one of these, a NASA speaker will discuss the origins of the item, the reasons why NASA undertook the work, the innovation that resulted, and the way it was used. Then Battelle staff members will speculate on the possible results of further directed research, the new uses that might be found, the modifications that might be made and/or the derivatives that might hold promise. Also, we will try to present the research that might lead to commercially attractive manufacturing methods, modifications that could improve fabricability, alternative raw materials, and other possibilities for cost reduction.

To serve as a case history, one has been selected that has been commercially developed. We will go into this a little more deeply. This presentation will cover the work that has been done to bring this particular class of products to the market place.

I would like to emphasize again--these are chosen to exemplify the method--to illustrate how others might explore the same NASA literature perceptively, looking for starting points for promising research and opportunities to capitalize on the work that has been done by doing more work! This is what we want to talk about today.

## RECENT CHANGES IN NASA PATENT LICENSING POLICY

Gayle Parker  
Counsel for Patent Matters  
Office of Assistant General  
NASA, Washington, D.C.

I have been with the NASA Office of General Counsel for about 11 years and have participated actively in the Technology Utilization Program but especially dealing with the legal problems associated with the transfer of this information. Throughout this conference we are going to discuss the utilization of the technology developed under NASA's aerospace research programs. Although approximately 19 other Government agencies are involved in research and development at taxpayers' expense, NASA has by far the most sophisticated program for the identification and the encouragement of the commercial utilization of the results of the agency programs.

NASA, as you may know, has been averaging between 4 and 5 billion dollars a year for the past 6 years in research and development activities. Over 90 percent of this work has been performed by private industry and the balance of roughly 10 percent has been done in-house in NASA or other Government laboratories. As you can well imagine, boxcars and warehouses of technical reports have resulted. It is quite a responsible piece of effort to sift through this information and to try and find out what information has potential use for the consuming public.

Separate from the technical reports that are submitted by our NASA employees and by NASA contractors, the National Aeronautics and Space Act of 1958, various presidential directives and executive orders require that individual inventions be reported to NASA. And again the same directives and the same statutory authority requires that the title to these inventions be held by NASA. There is a provision, however, and this in turn may come up later on in our discussion, where NASA, once it acquires title to an invention made by a contractor, has the right to waive title or at least the commercial rights in that invention back to the contractor who made it. Our term for this is a "a waiver of rights"--a waiver of commercial rights from NASA back to the contractor.

The same authority that gives NASA the requirement to obtain title and authorizes them to grant the waiver of some of these rights back to the contractors also requires NASA to obtain patent protection for the inventions for which it retains title and which are significant enough to patent. It also requires NASA to issue licensing regulations under which the consuming public, the industry, the firms and the individual organizations that want to use this technology may use the technology under a license agreement from NASA.

To give you an example of the magnitude of the problem that we are speaking about, during the fiscal year that ended June 30 of 1970 NASA obligated approximately \$4 billion for research and development work. During this same fiscal year, we received 410 inventions from our in-house employees and 2,632 invention disclosures from our contractors for a total of slightly more than 3,000 invention disclosures. Of those that we received from our contractors, 55 were waived back to the contractor. In other words, the

Government reserved the right to use them for governmental purposes, but the contractors were given the commercial rights to these 55 inventions. As you see, of over 2,600 inventions reported by contractors, 55 were waived back; the balance are owned by NASA. During the same year, NASA filed 318 applications for patents in the United States on 318 different inventions. During the same year, 250 patents were issued to NASA.

Some of this technology covered by this patent material that I have been discussing will be discussed today. Some of this technology has been made by contractors, some of it has been waived back to the contractors, and the contractors have the commercial rights. Some of these inventions were made by our employees within our laboratories. Some of them have been patented by NASA, and in some we have examined the state of the art and determined we were not the first inventors; we perhaps had just advanced the state of the art but the advance was not important enough to us to obtain patent protection for it.

As of today, NASA has title to over 1,800 issued patents in the United States. We currently have pending in the U.S. Patent Office patent applications for another 600 inventions. We are talking in terms of a data base here of about 2,400 patentable and patented inventions.

These inventions cover practically every field of technology with which we are principally concerned. As you can well imagine, a lot of this technology resulted from the manned space flight program. We had to keep the astronauts in good health. We had to provide methods and techniques for their food and for their drinking and for the air that they breathe and for their health and well-being. It was necessary to provide methods for remotely sensing their physical status, communications, power generation systems, new materials, high temperature materials, low temperature materials, fire-retardant materials. Communications that we had never really envisioned 10 years ago have been developed and have been very successfully used together with metal-forming techniques, new processing techniques and many, many more. Some of these have been patented. Some are covered by pending patent applications, and, of course, more will be patented by NASA. Several of our Presidents have said that these Government-owned inventions represent a valuable national resource and it has been determined by President Nixon just as recently as August 23 of this year that the Government under a new directive from him should undertake a very vigorous technology utilization program and use the patent system to do so wherever possible.

What is a patent? I am not attempting to be a professor and teach you what a patent is, but if we are talking about it perhaps we should figure out what makes a patent special. Article I, Section 8, of our national Constitution states that the Congress shall have the power to promote the sciences and useful arts by giving inventors the exclusive rights to their inventions for a limited period of time. As a result of this mandate, Congress instituted the United States patent system under which inventors or owners of inventions are given patent rights for a period of 17 years, monopolistic rights to exclude all others from making, using, and selling that invention. The consideration for that monopoly is that the inventor or the owner of that invention will make it publicly available to anyone. It is a two-way street. To encourage the inventor or the owner of the invention to publish the invention through a patent or otherwise, Congress will give him patent protection for a period of 17 years.

A patent owner really has about four prerogatives available to him regarding his use of that patent. After he gets the patent he can, of course - First, do nothing; it doesn't make him any richer or poorer; it doesn't change his outlook; he just gets the patent; he may hang it on the wall, he may put it in a filing cabinet; he may do nothing at all. Second, he may exercise his rights, which he has, to exclude all others from making, using, and selling the invention covered by that patent, if he should desire to do so. Third, he may license the patented invention to two or more other persons to use the invention, excluding all other people who are not licensed. This is nonexclusive licensing; and he may charge a royalty and he usually does. Fourth, he may choose to exclusively license it; in other words, choose one company which he thinks is the best company that he can rely on to make a success on the commercial market with that invention. Four prerogatives - (1) do nothing, (2) exclude all others, (3) grant nonexclusive licenses to two or more, or (4) grant just one license.

What is the value of a patent to a licensee? Principally, the value of a patent is that the licensee knows that as long as he has a license under a patent he can be reasonably sure that no one else is going to burden him with an infringement action or is going to bother him about infringing their patent. If he already has a license under the patent he knows that he has at least a right to proceed in the direction covered by that patent. He also knows that, if he has the exclusive rights, he has a right to exclude all others from making and using the invention. He has a protective device built in for his incentive to invest his time and money and effort to commercially develop the invention.

Up until 1962 it was Government policy to not really do anything with its patents or at the very most to grant some nonexclusive licenses, but really not to do anything with them. I said that was one of the prerogatives. However, beginning in 1962 NASA issued its first licensing regulations as required by Congress. NASA provided that NASA would grant nonexclusive licenses for its inventions. However, if it appeared that exclusive licensing was necessary, NASA would grant exclusive licenses where it was evident to NASA that such a license was necessary.

To date NASA has granted over 300 licenses for its patents and patent applications, both nonexclusive and exclusive. However, we have been doing this for 9 years. We have had a lot of experience. We have had more experience than any other Government agency. We were directly involved in the motivation of the actions of the President in having this story brought more definitively to the attention of the other Government agencies. The President did issue recently, as I said, in August, directives that licensing activities would be taken on a Government-wide basis.

NASA itself has just recently published new proposed licensing regulations, taking advantage of the experience we have had for 9 years. We have published these licensing regulations as proposed regulations on November 3, 1971, this year in the Federal Register. During the 30-day period up until December 3, we are receiving comments from industry and the public concerning our proposals. Soon after we evaluate the comments we propose to issue our new licensing regulations. The name of the game has definitely taken a very strong step forward in using patents for encouraging the transfer of this information.

I would like to read just two of the policy statements from our proposed licensing regulations. I must tell you that the Administrator of NASA told us when we were preparing these regulations that these regulations must serve the technology utilization program and they must be written from the viewpoint of the potential licensee. I shall read part of the policy considerations.

NASA inventions will best serve the interests of the United States when they are brought to practical application in the shortest time possible. Although NASA encourages the nonexclusive licensing of its inventions to promote competition and achieve the widest possible utilization, the commercial development of certain NASA inventions calls for a substantial capital investment which private manufacturers may be unwilling to risk under a nonexclusive license. It is the policy of NASA to seek exclusive licenses when such licenses will provide the necessary incentive to achieve early practical application of the invention.

The Administrator of NASA in determining whether to grant an exclusive license will consider the necessity for further technical or market development of the invention, the capabilities of the prospective licensee, their proposed plans to undertake the required investment and development, the impact on competitors, and the benefits of the license to the Government and to the public. Consideration may also be given to assisting small businesses and minority business enterprises as well as economically depressed, low-income labor-surplus areas.

As Mr. Burnett mentioned earlier, much of the NASA technology is in the NASA data bank. Our patents have been abstracted and are also in the NASA data bank and we have the unique capability of retrieving information regarding patents in any technical area where we have patent protection. NASA is taking a very giant step forward in encouraging companies to come in and obtain licenses from NASA to encourage technology utilization. Beginning in January, 1972, we will be publishing a semiannual bibliography of NASA patents available for licensing. It is called NASA Patent Abstracts Bibliography, but, in fact, it will also cover the 600 pending applications for patents. These will be updated every 6 months. The bibliography will contain an abstract and a drawing of every patent and patent application broken down into 33 technical categories. Anyone seeking information, for example, in the chemical processing field, will turn to a certain section and there they will be. Anyone seeking information in the electrical field will turn to that section and there they will be. Every 6 months a new publication will come out. Each publication will have six indexes which will be brought up to date and each issue will have an accumulative index so all of our patents and patent applications will be shown in the appendix of each index according to the technical field to which they relate.

In closing, I would like just briefly to say that very similar patent-licensing programs are being instituted by direction of the President in all Government agencies under the regulatory control of the General Services Administration. A number of the agencies have not moved forward, but under the direction of the President this will be done Government-wide. First of all, all inventions generally will be made available for nonexclusive licensing. This technology was paid for by the taxpayer and it really requires a serious consideration to take it from the taxpayer and to give, for example, an exclusive license to one company. We do know though through several years of experience that in some cases an exclusive license is



absolutely necessary to encourage and set up the incentive programs where a company will invest time, money, and effort to put the item on the commercial market.

The proposed technique is this - As soon as the Government files a patent application with the Patent Office the invention will be announced as available for licensing. Companies seeking licenses will make their application directly to the Government agency, in our case, NASA. Then, under the NASA regulations, 9 months after we make the invention available for licensing and if it is determined that it looks like that invention can be licensed non-exclusively to two or more companies, it will be licensed that way. However, if it looks that, after the 9-month period, the invention cannot be developed or won't be developed commercially without exclusive licensing, NASA will then grant an exclusive license to one company to use that invention. Exclusive licensing of Government-owned inventions protected by patents is becoming a very serious subject and one to which commercial users must give serious consideration if they want to use Government technology. If you use it and you do not have a license and the Government does not know you are using it, they can very well grant an exclusive license to your competitor under the patent; and, as I said earlier, your competitor has the right of exclusion; he can use the courts to bring an injunctive action against you for using this material without a license. The name of the game is exclusive licensing, or nonexclusive licensing in such a way that exclusive licensing is not needed.

Just in closing, this brochure that Jim Burnett brought down from Lewis entitled "Benefits for Mankind from Space Research" contains a large number of individual items that have been selected for inclusion in this booklet. Many of these items shown in the pictures are covered by patents and have been licensed. I commend this type of material to you; however, if you have information, or if you desire information regarding the licensing program of NASA, you may communicate directly with me regarding this material and we will provide you with a quick response to your inquiry.

## CASE HISTORY OF A SUCCESSFUL TRANSFER: HYSTL RESIN

J. F. Jones

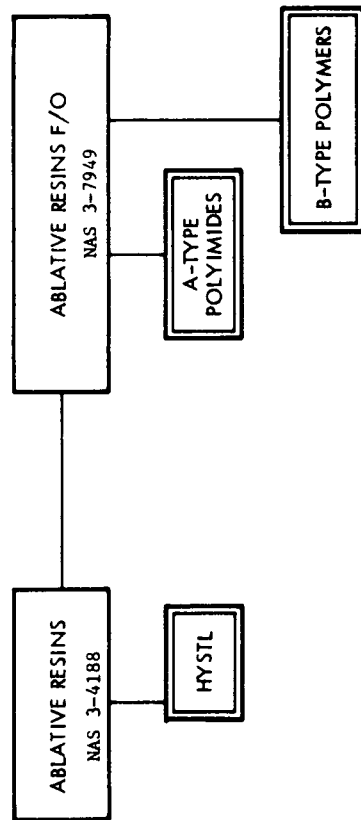
Head, Product Development Section  
TRW Systems Group, Redondo Beach, California

This presentation concerns the case history of HYSTL resins invented under a NASA contract, developed for several special uses during other NASA and Air Force contracts, but developed primarily for the commercial market by TRW Systems themselves. Commercialization was based on key inventions (which are very important in attempting to get into the commercial market). The HYSTL resin system has grown out of these key inventions, the primary invention being the composition of matter patent.

Let me describe the evolution of this resin system. Along the bottom of Figure 1 is an approximate time scale in years and shows the key NASA contract under which HYSTL was invented. Follow-on contracts have produced two other new materials: A-type polyimides, and new materials which we call B-type polymers (still under development and not ready yet to be discussed).

Looking more closely at HYSTL itself and the technology fallout from the key invention, you see across the top of Figure 2 a series of NASA contracts which utilized HYSTL resins in one way or another. These contracts we called the "NASA Bladder" contracts; in this particular case we mean positive expulsion bladders for rocket propellants. The idea at first was to make use of the tremendous chemical stability of the HYSTL resin while learning how to flexibilize it (HYSTL being a hard thermoset material). This approach was not successful; another key invention was made involving the use of HYSTL resin particles cocured with conventional elastomers (which produced the desired effect). This development ran its course through the NASA contracts and eventually (following the series of lines down and to the right) culminated in a series of current Air Force contracts (during which another key invention was made concerning HYSTL as coagents in elastomers). Further down, the boxes show the TRW efforts with HYSTL resins. The in-house commercial development lasted until the third quarter of 1968, followed by the business venture called the HYSTL Development Company.

Table 1 shows some of the key elements of HYSTL resins. They are based on the polymer 1,2-polybutadiene. Very key in the HYSTL 1,2-polybutadiene polymer is the high vinyl group content which needs to be above 80 percent of the number of unsaturated groups; the resins assay about 90 percent or better. Normally these materials are in the 1000 to 3000 molecular weight range, which means that they are liquids and thus readily processable. They possess reactive end groups (another key to the invention) which are hydroxy and carboxy groups. The resins are then chain extended through the use of materials which react with the end groups to form a higher molecular weight intermediate which is shelf stable. Finally, at a higher temperature, the intermediate is free radical (peroxide) cured to the thermoset material, which is either a massive cross-linked network, or a cyclization network, or both (we are not quite certain which).



1964	1965	1966	1967	1968	1969	1970	1971
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FIGURE 1. CHRONOLOGY OF MAJOR POLYMER TECHNOLOGY FALL-OUT FROM NASA ABLATIVE RESIN PROGRAM

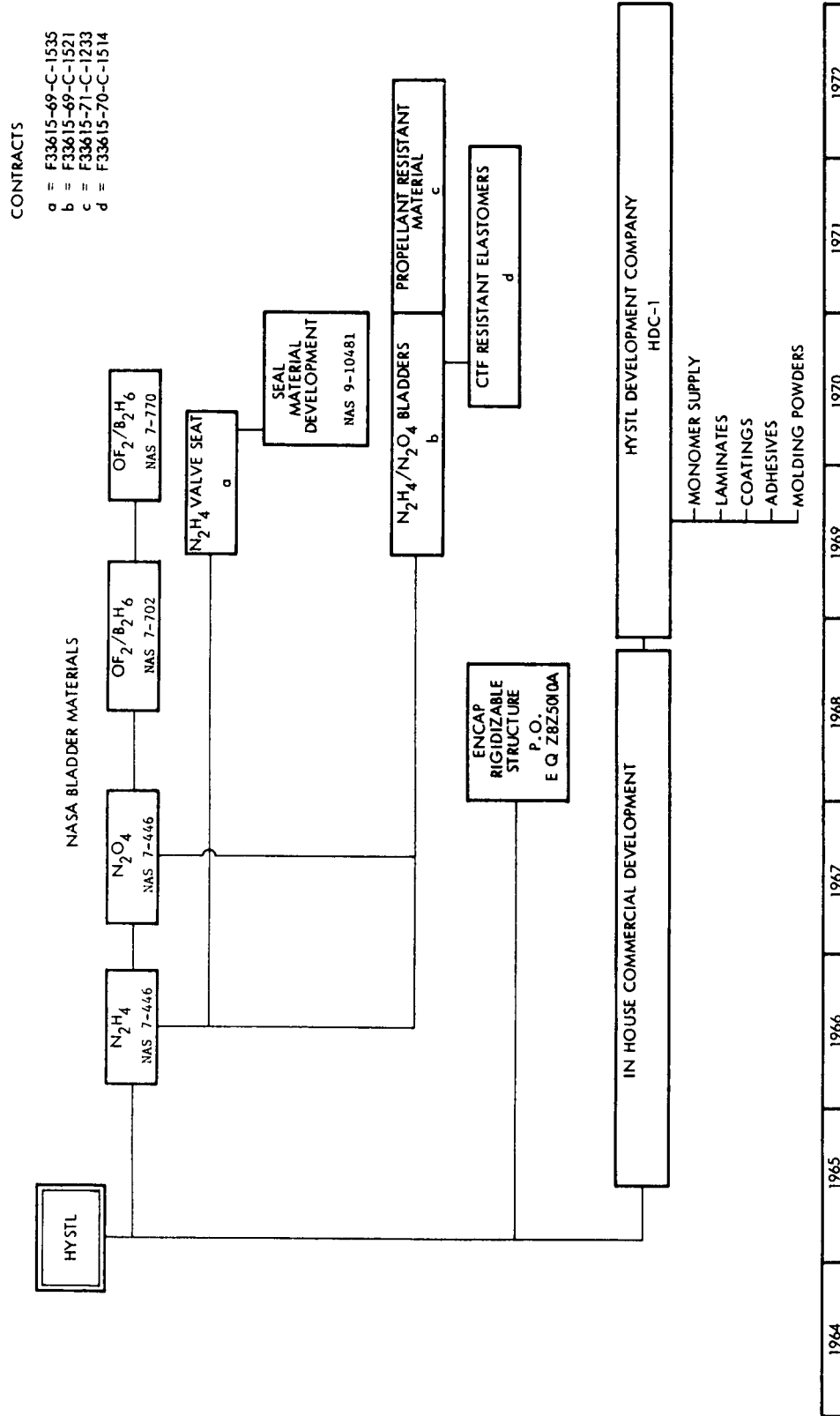


FIGURE 2. CHRONOLOGY OF HYSTL FALL-OUT CONTRACT AND COMMERCIAL DEVELOPMENT

TABLE 1. HYSTL RESINS

- Based on 1,2-polybutadiene liquid polymers
- Normally 1000-3000 molecular weight
- Possess reactive end groups (hydroxy and carboxy)
- Chain extended to high molecular weights to form intermediate stage
- Cured by peroxide (free radical) to 3-dimensional thermoset plastic

Figure 3 shows the general structure of the dihydroxy material -- the one called HYSTL G-series resin. Note, in brackets, the vinyl group which comprises the majority of the unsaturated molecular weight, and note the two hydroxyl groups on each end which are reactive with diisocyanates to form a urethane "B-stage" or intermediate form.

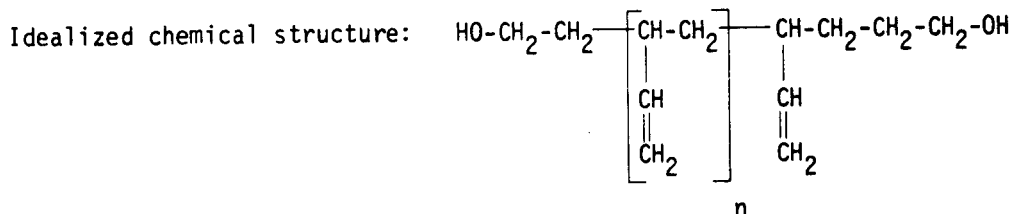


FIGURE 3. HYSTL G-SERIES (HYDROXYL-TERMINATED)

Figure 4 shows the same resin terminated with the reactive carboxyl groups. It can be chain extended in a similar manner; however, the choice of chain extension materials would be different.

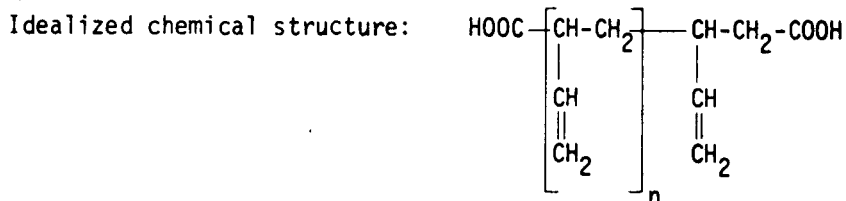


FIGURE 4. HYSTL C-SERIES (CARBOXYL-TERMINATED)

The hydrogen-terminated version is shown in Figure 5; this resin is actually outside the technology which was invented for NASA. However, this material is also available and we found that it is quite useful. (It has been the basis for some TRW-supported inventions.)

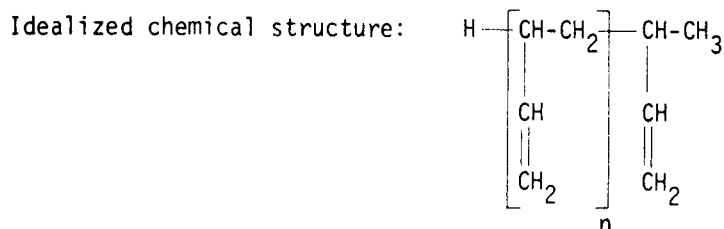


FIGURE 5. HYSTL B-SERIES (UNREACTIVELY TERMINATED)

Those materials comprise the three HYSTL resin types -- each one available in the 1000-3000 molecular weight range.

The key characteristics of HYSTL resin and the very reason that we thought to commercialize it are shown in Table 2. The chemical resistance is quite astounding. Since it is a hydrocarbon (somewhat analogous to a thermoset version of polyethylene); it has chemical resistance which approaches that of fluolocarbon polymers. (For instance, in liquid fluorine, it appears to be stable.) Electrical properties are typified by those of polyethylene and polypropylene -- low dielectric constants, low loss factors, and high dielectric strengths. It has the mechanical properties of epoxies and the thermal properties of some of the better epoxies (having a heat deflection temperature of about 490 F). Because of the unusual end groups, the resins are nearly unlimited to the kind of processing you can do with them -- even vacuum forming at thermoset conditions. The resins have a very high tolerance for a wide variety of fillers; having both a low specific gravity (about 1.05), and also being rather liquid allows addition of considerable volumes of filler (more so than most resins will tolerate while still providing excellent strength and strength retention; this is a very important commercial advantage). HYSTL resins have a high potential for use in a variety of product forms -- molding compounds, laminates, etc. The last item listed in Table 2 shows that HYSTL resins had a high potential for patent protection, and this, of course, was key in deciding whether TRW was going to invest capital in a commercial venture.

Figure 6 is a very simple diagram showing essentially how the HYSTL resin system intermediate form was envisioned to be put together. Simply, the liquid resin is mixed with the various materials. The sheet (a possible sheet molding compound) is then put into the oven and the intermediate stage created. If it happened to be a urethane-type chain extension, the intermediate was more or less a urethane elastomer at that point. The finished "compound" was then ready for final processing into end products by putting it in a molding press (or whatever), and finishing the cure at the higher temperature. The peroxide remained in situ in the intermediate stage and reacted at the higher temperature forming the hard thermoset part.

TABLE 2. KEY CHARACTERISTICS OF HYSTL

- Chemical resistance approaching fluorocarbons
- Electrical properties of polyolefins
- Mechanical properties of epoxies
- Thermal properties of better epoxies
- Processability nearly unlimited to type
- Tolerance for wide variety of fillers - very high
- High potential for variety of product forms
- High potential for patent protection

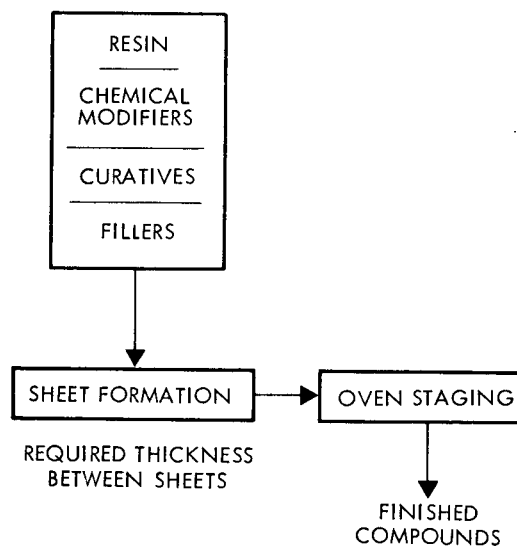


FIGURE 6. HYSTL RESIN SYSTEM INTERMEDIATE FORMS

On the basis of the foregoing information, we began a preliminary market survey. TRW Inc. is a large and diversified company. The primary source of information for our initial market survey came from some of the operating groups at TRW -- Automotive, Electronics, etc. We put together a survey, Table 3, which looked excellent. The primary utility of HYSTL resins was going to be in specialty applications, not high volume, commodity materials like polyethylene. We had a combination of physical and processing properties which were unique, but for any single given property, there was a competitive material; e.g., looking strictly at HYSTL resins for chemical resistance, wouldn't Teflon do a better job? There was some quandary about exactly into what slot(s) HYSTL resin would fit. To obtain the answer was one of the major tasks at that point -- to develop sufficient numbers of physical and mechanical properties to determine just where it would best fit and, in turn, whether it was really suitable for a commercialization venture. At that time quoted resin prices were in the \$2 to \$5 per pound range from producers here in the United States.

TABLE 3. PRELIMINARY MARKET SURVEY

- Primary utility in specialty applications
- Combination of physical and processing properties defined unique character but pointed to wide variety of potential competitive plastics for each of HYSTL's strengths.
- Necessary to provide initial product form properties to define "slot" in which HYSTL would compete
- Probable \$2-\$5/lb resin cost (high volume, U.S.)

An initial product development phase was carried out in which we looked at both filled and unfilled HYSTL resins. Figures 7 and 8 show the sorts of comparisons made -- the various strengths and electrical properties. HYSTL resin, in most cases, was better than the materials we chose to compare them with. We did not choose the worst material in the case of the epoxy or the polyester, or whatever we were comparing with. We chose the competitive compounds we felt were the best. The comparison was impressive. It gave us faith that we should go on with this venture.

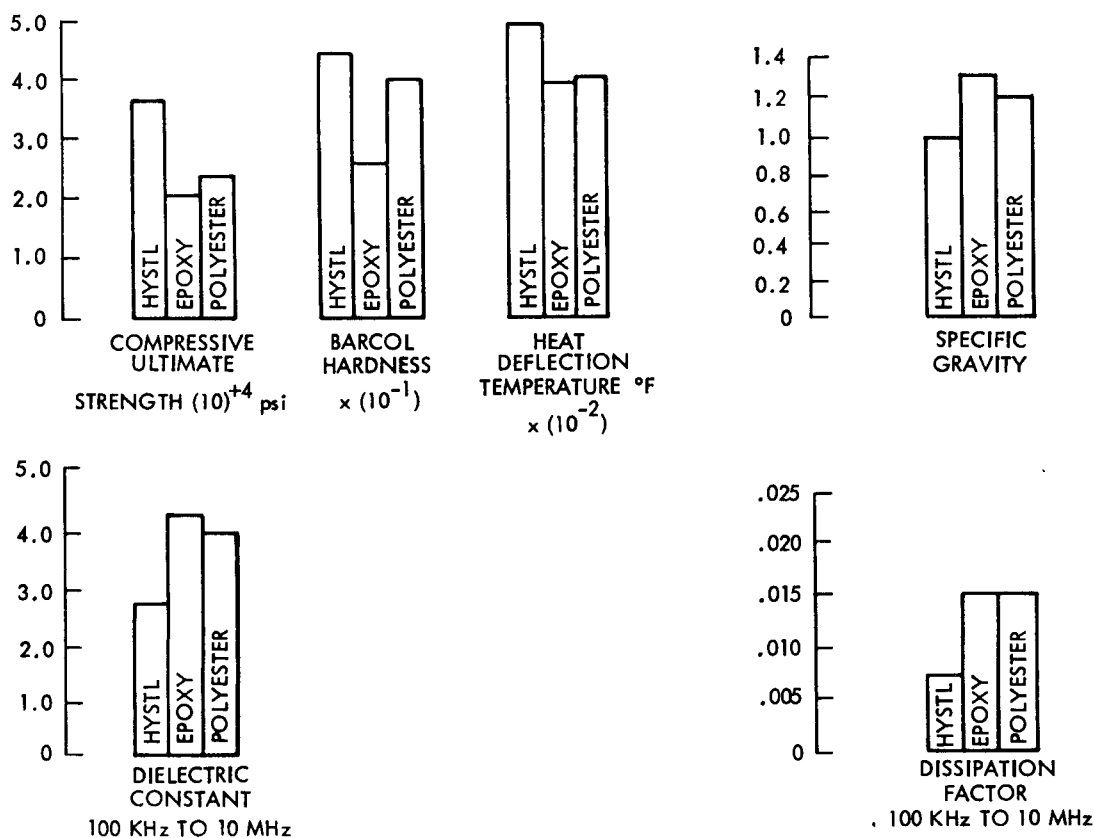


FIGURE 7. COMPARATIVE PROPERTIES OF UNFILLED HYSTL RESIN SYTEM



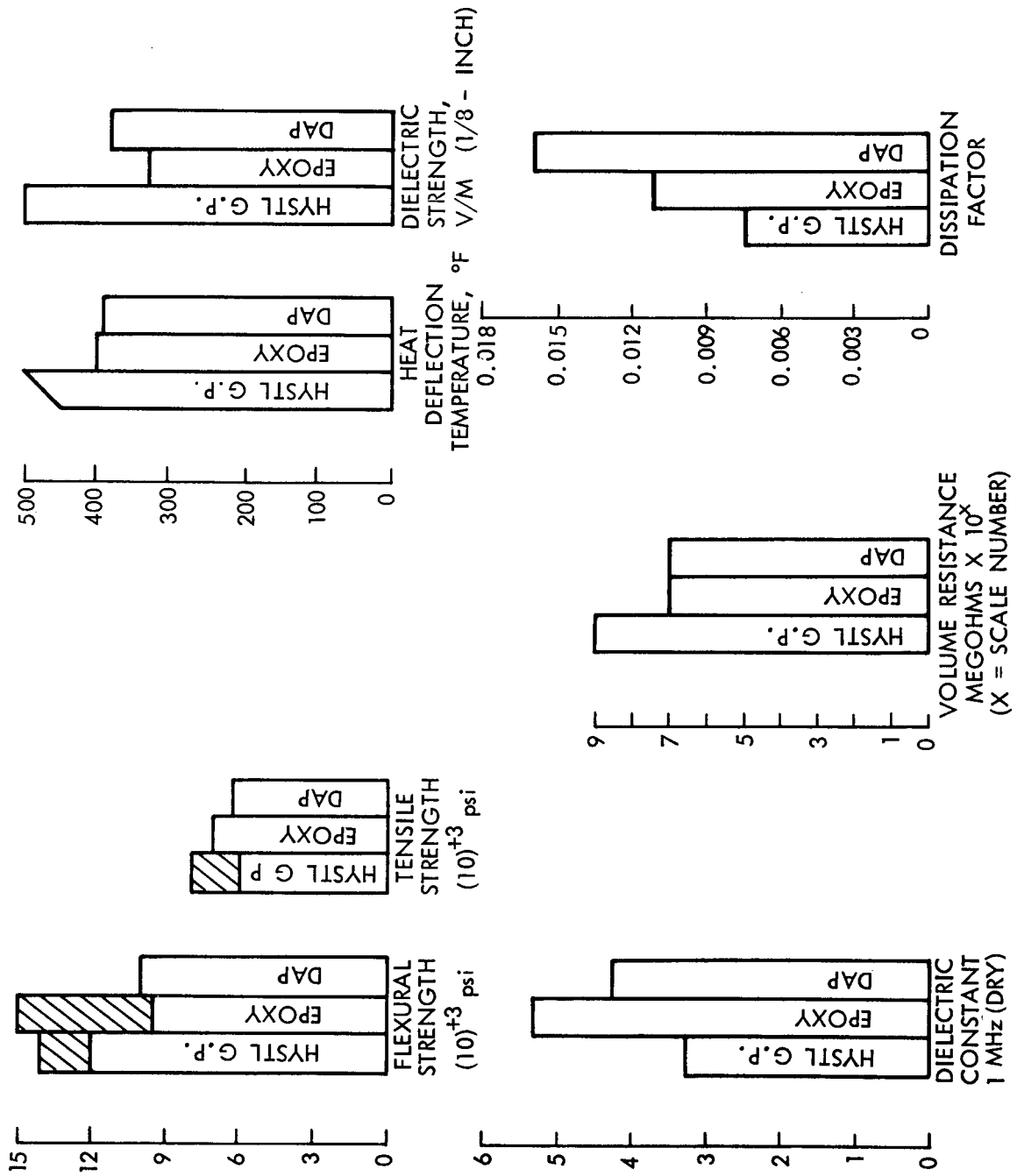


FIGURE 8. COMPARATIVE PROPERTIES OF HYSTL GENERAL PURPOSE MOLDING COMPOUNDS

On the basis of that preliminary comparison, which looked quite heartening, we elected to do a major market survey. At this point in time, since we were anticipating a considerable investment, it was necessary to get as much marketing information as possible to determine the market size and the market price. The basis for the survey was the information which was just presented -- those preliminary product form properties. Table 4 outlines the results. The markets which were identified told us that HYSTL was a valuable addition to the plastics industry. However, it did have a limited market as you might expect (being a thermoset material), there would be competition (and that was good), market development would be lengthy because of the brand new nature of the material (selling people on an entirely different concept in both material and processing); areas for the material (at least near term), and any sales attempted should concentrate in the specialty areas (which we had already suspected from the preliminary market survey).

TABLE 4. MAJOR MARKET SURVEY

- Basis: Preliminary product form properties
- Markets:
  - A valuable addition to the plastic industry
  - Limited market compared with thermoplastics
  - Competition will exist
  - Market development will be lengthy
    - Industrial moldings
    - Electrical components (insulation)
    - Corrosion resistant pipe, fittings, etc.
  - Sales should concentrate in specialty areas
- Economics:
  - Resin price should be in \$0.75-\$1.50 range
  - Business venture should consider
    - Acquisition
    - Licensing
    - Joint venture
    - Internal

Key Conclusion - No venture palatable without large volume supply of \$0.75-\$1.50/lb resin.

So far as the economics are concerned, Table 4, the price at which HYSTL resin would begin to make a profit [which is rather important in a commercial venture] was in the \$0.75 to \$1.50/lb range (well below the quotations we were then getting from U.S. suppliers). A business venture to provide production and marketing would probably be required which could be in any one of four forms - (1) acquisition, (2) licensing, (3) joint venture, or perhaps (4) TRW internal. But the key conclusion to be made from the rather extensive market survey was that the \$0.75 to \$1.50 per pound price range was critical, and that it was necessary to get down into that particular range in order to be successful. Otherwise, it was simply not a palatable commercial venture.

Table 5 outlines the approach taken. About the end of 1968, a new company was formed called the HYSTL Development Company, HDC (a joint venture between Commonwealth Oil and Refining Co. of Puerto Rico and TRW Inc.). A near term source of resin was located, the Nippon Soda Co. of Japan (who had technology in the polymerization of butadiene); they were willing to sell it to us in the desired price range. This was key, of course, in going ahead. For the long-term supply, CORCO had interests in utilizing butadiene (which they had as a by-product of their petroleum streams) and TRW Systems was interested, both in continuing the R&D work and also in taking over (at least at that point in time) sales, management, marketing, etc.

TABLE 5. HYSTL DEVELOPMENT COMPANY  
A JOINT BENTURE BETWEEN TRW, INC. AND CORCO

Basis:

- Source of near term resin supply (less than \$1/lb) located and arranged (Nippon Soda Co., Japan)
- Long term supply - plant to be built by CORCO
- R&D, sales, marketing and product development - TRW Systems

In Figure 9 you see the organization with which we started, where the object was (1) to have CORCO (who was in the butadiene business) as a partner, and (2) vertically integrate (which was an interest of CORCO's management at that time -- a corporate goal) into the "tier one" type activity, in a period of 5 to 10 years (whenever CORCO could get a prepolymer plant built). Nippon Soda was considered at that time a source of supply for the near term. It was an additional goal to vertically integrate the HYSTL Development Company into "tier two" type activities which involved actual manufacture of product forms. This has happened to some extent.

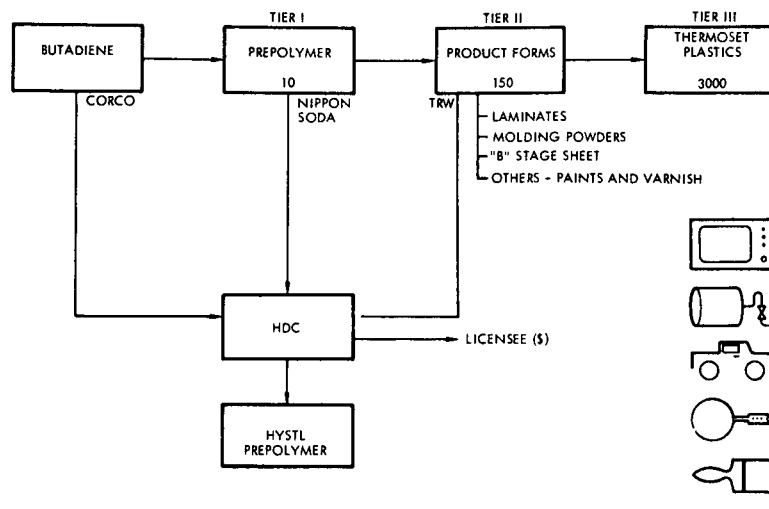


FIGURE 9. MATERIALS FLOW

[It is necessary to interject the following at this point. As a result of the business recession about a year and a half ago, CORCO was required to abandon the HDC joint venture due to considerations for their major product lines. TRW has elected, however, to continue the work, and the HYSTL Development Co. still exists essentially in its original form.]

Returning now to the major point, the lower right corner of Figure 9 pictures the markets that we had identified -- electronics, chemical processing, automotive, appliance, and coatings. They all looked very attractive at that point in time.

The major task was to go into a product development phase for which we at TRW were contracted by the HYSTL Development Co. This was carried out in conjunction with, and more or less simultaneously with some of the NASA and Air Force contracts. Technology that TRW was developing was being fed into the government programs. Technology which came out of the government programs as key inventions was being utilized as a basis for further commercialization in HYSTL projects. Table 6 shows two prime areas for fast market penetration - molding compounds, primarily in the electrical industry, and laminates, again in the electrical industry or aircraft industry in the case of radomes. As it turned out, the laminate area was much slower to develop. The molding compound was an accurate projection on our part.

TABLE 6. PRODUCT DEVELOPMENT

AREAS OF FASTEST MARKET PENETRATION IDENTIFIED

- Molding compounds
  - Electrical components
- Laminates
  - Circuit boards
  - Radomes

Other market areas, shown in Table 7, were seen as not capable of getting very fast results, but nonetheless something that should be worked toward -- molding compounds again (but for slightly different applications), laminates, adhesives, and coatings; these four areas have been extensively developed at this point in time.

The results were very interesting after sampling potential customers. There were some discouraging things as well as some good things. Referring to Table 8, the shrinkage was too high for most applications, particularly electrical encapsulation. The flow was too hard. Customers wanted granular compounds as opposed to dough-type molding compounds. Retention of properties, they said, was too low at 300 F. However, many customers did say that the HYSTL molding compounds had the best room temperature properties that they had seen. Chemical resistance and shelf life were excellent. They found excellent electrical properties; however, the laminates that we presented did not pass the "water boil" test. (They came apart at the seams.)

TABLE 7. PRODUCT DEVELOPMENT  
AREAS WITH HIGH POTENTIAL MARKETS

- Molding compounds
  - Corrosion resistant pipe, fittings, etc.
  - Electrical encapsulation (molding)
  - Automotive (mechanical/electrical/thermal)
- Laminates
  - Aircraft
  - Automotive
  - Marine
- Adhesives
  - Rubber to metal
- Coatings
  - Chemical resistant
  - Electrical insulation

TABLE 8. REPORTS FROM THE FIELD

- Shrinkage too high
- Flow too hard
- Want granular, high flow molding compound
- Retention of properties too low at 300 F
- Best room-temperature properties available
- Excellent chemical resistance
- Excellent shelf life
- Excellent electrical properties
- Laminates do not pass water-boil test

Another key invention was made and developed primarily by HYSTL Development Co. under their own funding -- a way out of those problems. Table 9 shows the new concept: new block polymers or copolymers, where, instead of using the diisocyanate system (with which we had difficulties particularly in shrinkage and water resistance), a new chain extension system was utilized. This consisted of the attachment of acid anhydrides to the hydroxyl groups on the end of the G-series resins in a reaction-type vessel. Then, by the normal techniques, the utilization of epoxy resins (low molecular weight materials in most cases) to act as the chain extender instead of the diisocyanates. The new approach provided a more polar material in a more or less "block polymer"

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fashion. It provided the solution for which we were looking. The shrinkage went down; the water resistance went up. It was the major solution to many of the problems which we saw as major difficulties of getting into the marketplace.

TABLE 9. NEW BLOCK POLYMER CONCEPT

Objective

- Reduce brittleness of HYSTL resins by chain extending with tough copolymers.
- Improve adhesion to reinforcement by use of highly polar copolymers.

Solution

- Use acid anhydrides and epoxy resins as copolymers for chain extending HYSTL resins.

I want to describe some of the compounds which have been made and look interesting at this point in time. Granular and dough-type molding compounds of HYSTL have those features in Table 10. Figure 10 shows what we were attempting to get earlier and could not -- the granular-type material. Table 11 describes sheet molding compounds primarily for automotive use, the kinds of materials the automotive companies are using now to make tail light extensions and spoilers on the rear end of automobiles. Figure 11 shows some laboratory versions of sheet molding compound forms. The automotive paint baking cycle, which was the major drawback to less thermally stable materials such as polyesters, can be overcome by use of HYSTL materials. The figure also gives an indication of the flexibility which these sheet materials have -- one material being the intermediate stage (which is quite drapable) and the rigid section molded between the two aluminum angles.

TABLE 10. HYSTL GRANULAR AND DOUGH MOLDING COMPOUNDS

Features:

- Easy processing (compression or transfer)
- Fast cure
- Excellent mechanical, thermal, electrical and chemical properties combined
- Shelf-extinguishing versions developed.

Table 12 describes a special high impact strength material. The material displays high impact strength, approaching or perhaps surpassing the impact strength of Lexan and yet is a thermoset material. It also has tremendous impact absorption ability. We have a number of interests in this. The fact that it retains its high chemical resistance makes it a very interesting candidate for battery cases and at low cost. Figure 12 shows molded parts which we use for testing in our laboratories.

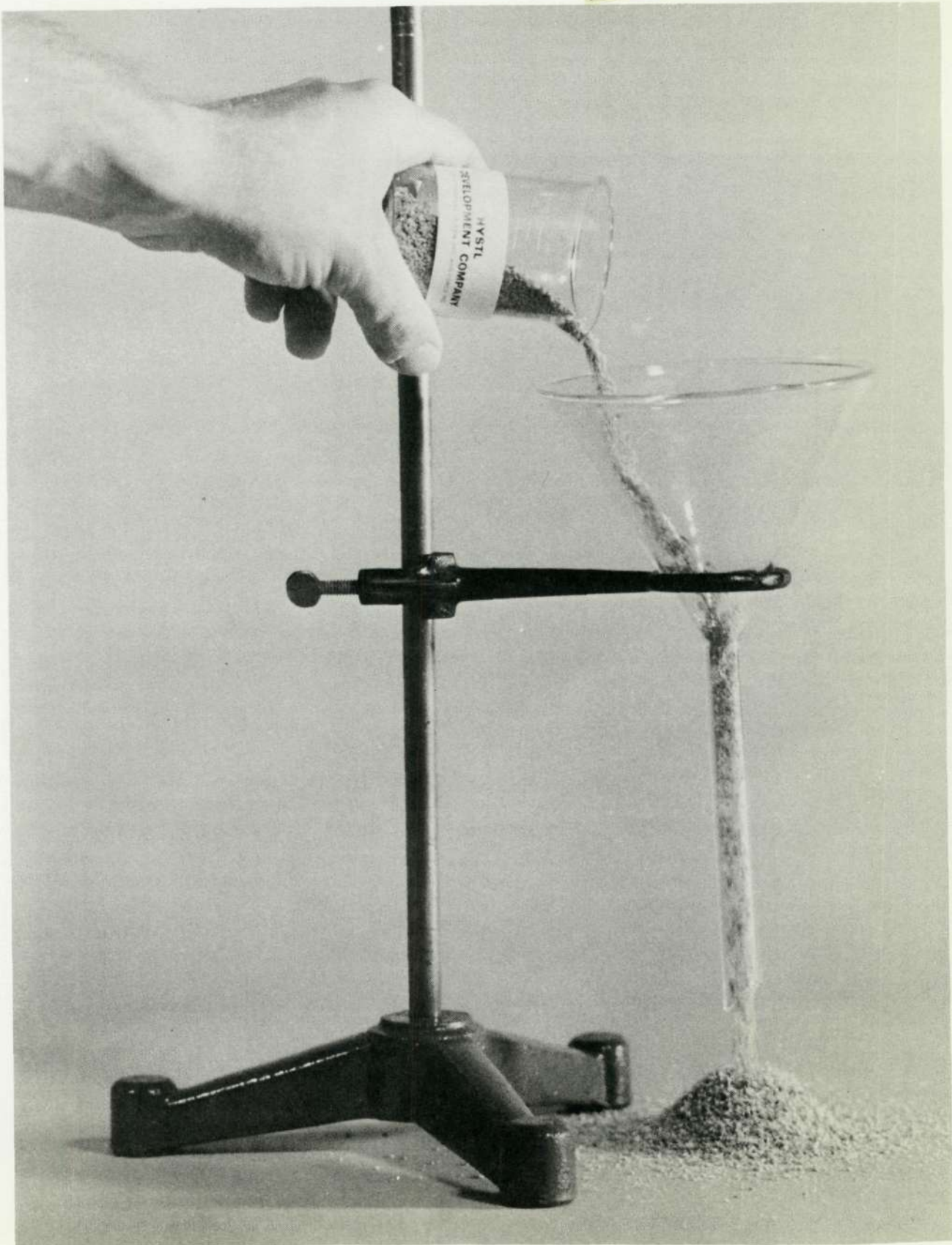


FIGURE 10. GRANULAR, FREE FLOWING HYSTL MOLDING COMPOUND



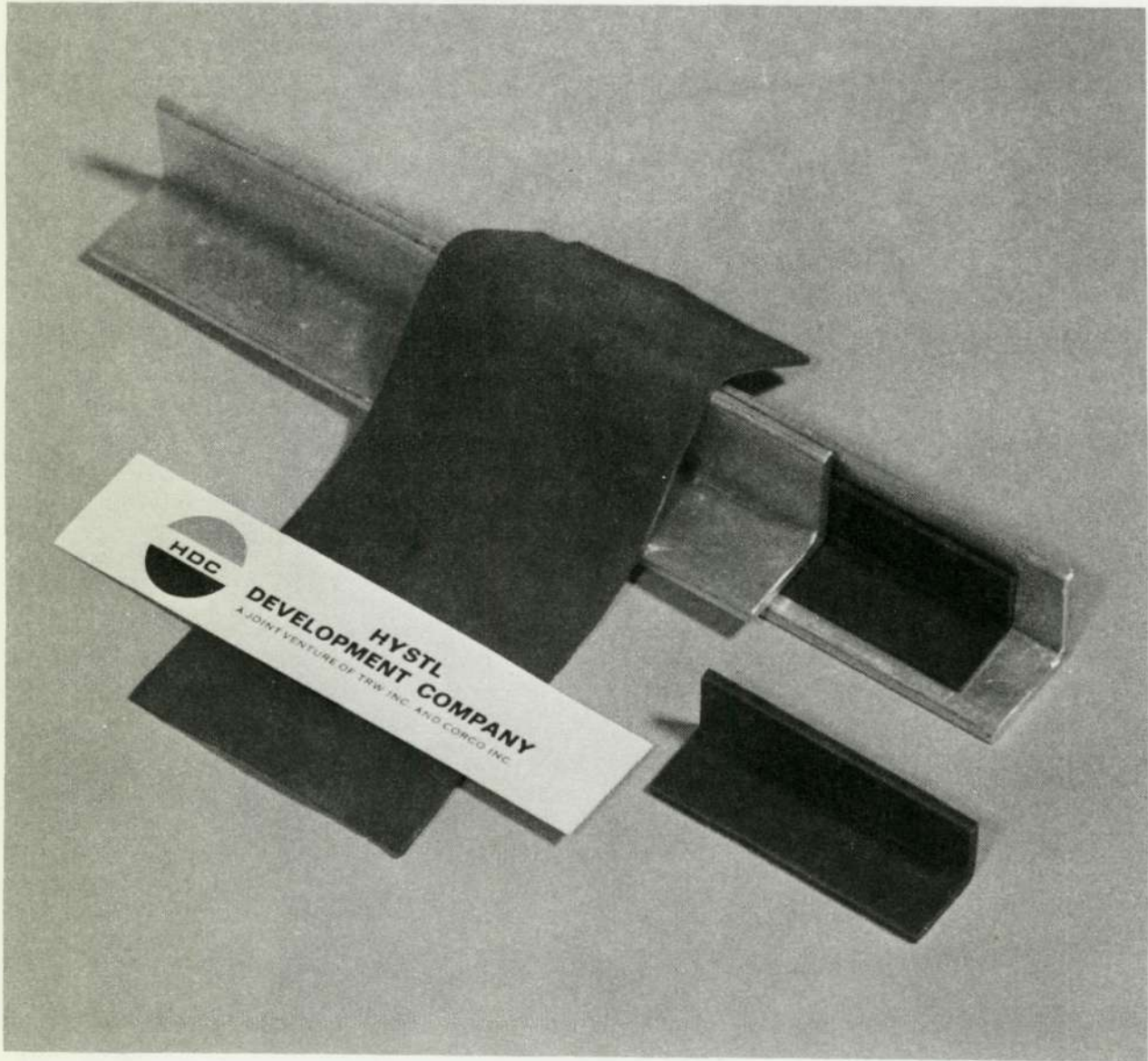


FIGURE 11. HYSTL SHEET MOLDING COMPOUND



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FIGURE 12. MOLDED HYSTL TEST BARS

TABLE 11. HYSTL SHEET MOLDING COMPOUNDS

## Features:

- Fast processing
- Good dimensional/thermal stability (capable of withstanding paint baking cycles up to 400 F)
- Paintable
- Cost competitive (\$0.40-\$0.50/lb) with polyesters and epoxies

TABLE 12. HYSTL SPECIAL HIGH IMPACT STRENGTH MOLDING COMPOUND

## Features:

- High impact strength and energy absorption between -20 F and +250 F
- Easily processed
- Compatible with battery acid
- Low cost (\$0.006/cu in.; \$0.12/lb)

The area of laminates did not proceed quickly until we had the block copolymer concept. However, once having done that, the features shown in Table 13 have renewed our interest in this area.

TABLE 13. HYSTL LAMINATES

## Features:

- Compatible with wide variety of reinforcements
- Easy processing, fast cures
- Excellent mechanical, thermal, electrical and thermal properties combined

Hystl Adhesives for Rubber Bonding

## Features:

- Co-curing adhesive coatings for mold/bonding rubber to metal
- Tested bond strengths exceed strength of rubber.

Table 13 also describes adhesives for rubber bonding -- a very interesting phenomenon. The fact that HYSTL is peroxide cured and that it contains unsaturation makes it a natural candidate to cocure easily with many elastomers. In the chain extension portion of it, where it contains the very polar epoxide linkages, it makes a good adhesive to metal. The two segments of the polymer, if you will, create a tremendous interface for a rubber-to-metal bond. In most of the cases where tests were performed the elastomer failed before the adhesive.

HYSTL and elastomers -- I mentioned earlier that HYSTL resin as a coagent in elastomers was another key invention. The effects that HYSTL has on an elastomer are very interesting, Table 14. Since it is a liquid, it acts as a plasticizer before the cure, much in the way a process oil does. However, after it is cocured it turns to its hard, thermoset state and acts as a reinforcing agent (as carbon black would and which a processing oil cannot do). It is not scorchy -- rather, it has a very high tolerance for temperature, and the rubber does not cure prematurely. It develops a high cross-link density in the elastomer, thus both increasing the modulus (which is sometimes desirable) and decreasing volume swell in fluids. It considerably changes the compression set properties (of elastomers with which it can be coreacted) typically from a 50 percent level down to about a 10 percent level -- quite a significant change. It is economical to use and provides high-performance compounds.

TABLE 14. HYSTL WITH ELASTOMERS

- (1) Plasticizer before cure
- (2) Reinforcing after cure
- (3) Not "scorchy"
- (4) High cross-link density
- (5) Resists compression set
- (6) Economical high-performance compounds

Figure 13 shows a small rubber mill which we use for manufacturing small batches of rubberm as an indication of the sorts of things we have been doing with HYSTL resins.

Figure 14 shows ethylene propylene diene monomer material or where percent volume of additive versus the equilibrium swell in MIL-H-5606 hydraulic fluid at a temperature of 275 F. The graph shows the classic case of glass beads (which are put in to show the effect of volume dilution without reinforcement). Notice that, as more glass beads are added, the volume swell goes down slightly. If oil is added, the volume swell goes up. That is because the oil interferes with the cross-link density of the elastomer and makes it more susceptible to swelling. If silica or carbon black are added (the normal reinforcements) typical curves are generated showing some synergism from reinforcement in addition to volume dilution. Notice that the line for HYSTL resin shows quite a significant difference -- a small amount of material having gone a long way by reducing the volume swell from nearly 240 percent down to about 50 percent. This is simply one illustration of the kind of effect that HYSTL resins have on elastomers.



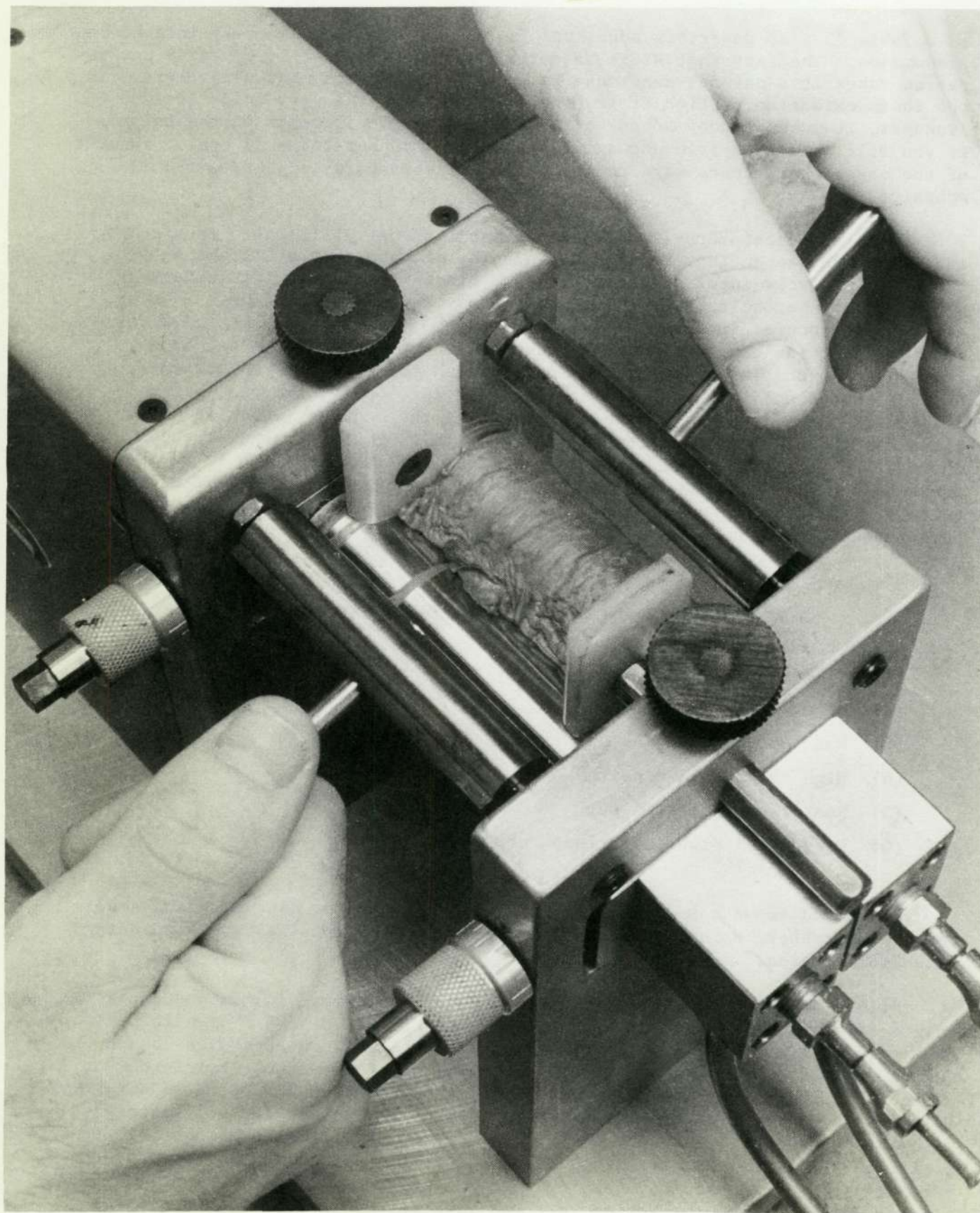


FIGURE 13. HYSTL CONTAINING ELASTOMER ON MICROMILL

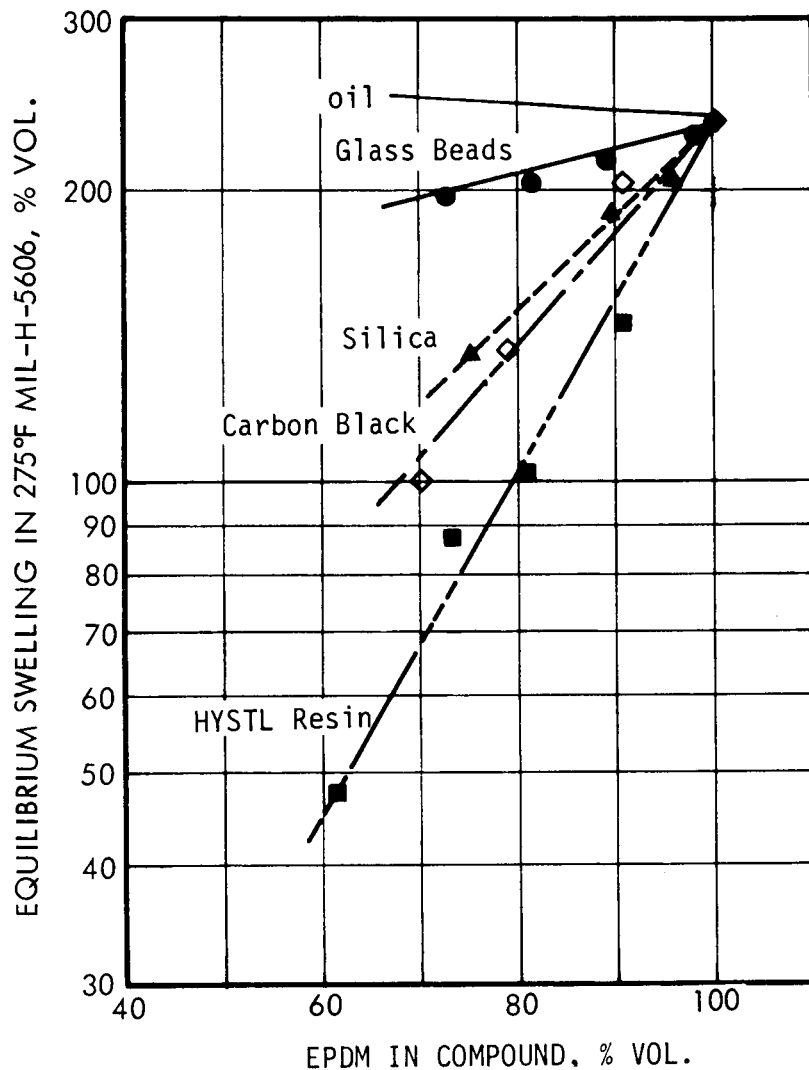


FIGURE 14. EFFECT OF FILLERS ON EPDM CROSS-LINK DENSITY MEASURED BY SWELLING

The last thing that I want to discuss is an application of HYSTL resin's natural chemical resistance. Since we are talking about technology utilization, certainly one of the largest benefits to mankind would be technology transferred to the medical arts. Chemical resistance provides potential for this material in three particular areas shown in Table 15. There have been some tests performed exploring the potential by well-known experimenters at the UCLA Medical Center. They have reported that the potential is high for the use of HYSTL materials, particularly for a shielding material for an implanted pacemaker for an artificial heart, or for the various things that they take out and replace these days.

TRW and UCLA made a film which shows one experiment that was performed at UCLA on implantation and removal of a HYSTL material in a laboratory rat. At UCLA's Medical Center, one of their primary tasks is to study the effect of various synthetic materials on tissue. Almost all nonbody-type materials will

TABLE 15. HYSTL IN MEDICAL APPLICATIONS

Potential being explored for:

- Replacement of damaged or diseased joints
- Bone replacement
- Protective sheath for implants

irritate internal organs or tissues of the human body. A small piece of unfilled HYSTL resin was implanted in the rat. Following the removal of the resin, two small pieces of tissue were put aside, which were in contact with the resin during the entire exposure period. The tissue was very carefully studied after the biopsy. It was reported that less effect from the HYSTL resin was seen on the tissues (various kinds of cell formations, giant white cells, etc., which form in the presence of some foreign body) than for almost anything else they had tried implanting up to that point. That is not conclusive, and does not imply you should run out and have a hip bone made out of HYSTL. Nonetheless, it was a large step forward in showing the utility of HYSTL resins in a medical application with potential benefit to mankind.

## POSSIBLE FUTURE DEVELOPMENTS

Gilbert M. Gynn  
Battelle, Columbus Laboratories

Before getting into the heart of my speech, I would like to spend a few moments reflecting on Mr. Jones's talk. I'd like first to thank him for bringing to us a most a most interesting account of the development of a new family of polymeric materials; an account which highlights a successful transfer of technology spawned under contract at NASA. The progressive development of Hystl resin chemistry is an excellent example of the methodology that can be followed to make use of profit opportunities which are available as the result of NASA-sponsored research.

As Mr. Jones has clearly shown, TRW and its jointly owned Hystl Development Company have taken the development of Hystl resins far beyond the stage reached in the original contract work. In fact, when I first learned that I was to speak on the subject of possible further developments of Hystl resins, I argued that the area had already been researched thoroughly by that company. However, after reexamination of the Hystl resin picture, I found that, indeed, as Mr. Jones has pointed out, the Hystl resin development really opened another door of synthetic polymer chemistry. As he indicated, a rather basic concept had evolved--that of preparing a low-molecular-weight polymer capable of chain extension through one mechanism and final curing through another.

Although our friends from TRW have made excellent use of this concept, I believe that they will be the first to agree that the work to date has proved out the concept but has not yet fully explored the possibilities for obtaining other polymer products with profit potential. What I propose to do then, during the next few minutes, is to speculate on what other materials may result from this rather basic development. I realize that some ideas I will discuss are, or have been considered, by TRW. Mr. Jones may wish to comment on these later during the question and answer period.

Success in speculation, whether in research or in more direct financial ventures, depends on having a solid base of information from which to work. Mr. Jones has given us that base. He has shown that a variety of thermosetting polymers can be prepared by linking "high vinyl" polybutadiene segments with diisocyanates, anhydrides and epoxides, and then curing the resulting polymer through the pendant vinyl groups. The polymers produced have shown excellent processing characteristics and a good balance of physical properties.

Some of the outstanding properties include stability to chemical reagents, outstanding electrical properties, high resistance to abrasion, low absorption of water, very high heat resistance, and excellent mechanical properties. The properties are, of course, dependent on the chemistry of the polymer (link up moiety) and the high degree of vinyl unsaturation capable of cyclizing, cross-linking, etc. Based on that specific knowledge of these materials, and general patterns that have been established between polymer

types and their properties, one may speculate about possible further developments. One may choose to use different chain extenders, modify the chemistry of the starting low-molecular-weight polymer, examine various cross-linking approaches, or combinations of all three. Let us first consider the use of other chain extension agents. One of the first possibilities that comes to mind is the development of a family of thermosetting polyesters. Although direct polyesterification is not easy with unsaturated diols, we have, at Battelle, shown in related work that it is possible in certain cases if a suitable catalyst is employed. A whole series of polyesters would be possible based on the reaction of monomeric or polymeric di-acids, acid chlorides or esters and the hydroxy- or carboxyl-terminated polybutadiene. One can speculate that the resulting polymers could be superior to the polyesters now in use with respect to physical properties, heat, light, and weather resistance. One polymer which I think would be of interest could be prepared by reacting the bis(chloroformate) of bisphenol A with the hydroxy-terminated polybutadiene. This would introduce the chain stiffening effect of the aromatic carbonate linkage. This idea could also be carried to the extent of preparing a block copolymer to achieve high toughness and hardness - a combination that is normally difficult to obtain.

Speculating about other possible useful materials that could be developed for profit, one should keep in mind the needs of the marketplace. As we will hear later in this seminar, there is a need for fire-resistant materials. One can speculate that through the proper selection of a chain extender such as an organo-phosphorous compound, one could produce a thermosetting material with inherent flame resistance.

Silicone and silane polymers have found wide use, yet it would be desirable if a more easily curable system having improved tear and abrasion resistance could be developed. It would be quite interesting, I believe to prepare a polymer or block copolymer of an organo-silane and the hydroxyl-terminated polybutadiene.

Mr. Jones has shown that polymers having very high chemical resistance can be made. I would judge that it should also be possible through the right choice of chain extenders to build links that would be subject to biologic, hydrolytic or radiation attack. Thus, if desired, one could probably build in a biodegradable feature.

It appears possible that one could formulate the chain extension moiety to impart photosensitivity. Perhaps a polymer could then be made to cure through the application of radiation -- useful for applications where heat would not be desirable.

It should be possible to introduce polar chain extenders, perhaps polymeric, that would greatly enhance the adhesion characteristics and broaden the use in that application area.

One can speculate that the carboxyl-terminated polybutadiene could be reacted with monomeric or polymeric diamines to prepare a family of cross-linkable polyamides.

As I indicated previously, it should be possible to prepare other polymers through modification of the low-molecular-weight polybutadiene.



This could be through copolymerization, or through modification of the polybutadiene itself. For example, it should be possible to alkylate the backbone at the tertiary hydrogen positions.

Still another approach for further developments would involve alteration of the cross-linking or curing characteristics. For example, through the addition of cross-linking agents such as triallyl cyanurate, one could possibly extend the heat resistance of the material. Alternatively, one might consider the possibility of partial hydrogenation of pendant vinyl groups to reduce the cross-link or cyclization density to yield a more thermoplastic material.

In conclusion, the development of a material for a specific application, such as has been done many times for NASA, means that certain properties were developed in that material - strength, heat resistance, etc. This development may be nearly directly translated to consumer use in some cases, while in others, further research is needed. Hystl resins exemplify the possibility of expanding a basic specialized development through further research effort into materials useful for a number of applications.

On first exposure to some NASA technology, it may appear to you that it is much too specialized or, as I first felt of Hystl resins, thoroughly worked over with little room for further development. However, as I have tried to point out with a few examples, there is still ample room for further developments of potentially profit-making materials.

## NONFLAMMABLE CELLULOSIC MATERIALS DEVELOPMENT

Matthew I. Radnofsky  
NASA Manned Spacecraft Center  
Houston, Texas

Introduction. Since the inception of the manned spaceflight program, NASA has been actively engaged in the development and utilization of non-flammable materials. This NASA activity, conducted with the assistance of industry, has led to a progression from the relatively unsophisticated flameproof materials available 10 years ago to the great variety of fibers, cellulose, elastomers, and composites that can now be fabricated into nonflammable items. The capability for fabrication, of course, involved the development of technology necessary to evaluate and to use properly the specialized materials now available. It is believed that many of the nonflammable and fire-resistant materials and much of the supporting technology developed for spacecraft usage can, when properly adapted, make a significant contribution toward achieving fire safety in the military, in construction and transportation industries, in public services, and in domestic and institutional services. In this article we are limiting our discussion to nonflammable cellulosic material developments.

Early Material Development and Testing. Early in 1967, after the setback in the Apollo program, we began a critical evaluation of flammability of materials. Some of the earlier materials examined and tested included Nomex paper from Dupont, W. R. Grace paper (vermiculite), and mica paper (ACIM Paper Corporation) developed under NASA contracts. These programs yielded nonflammable products; however, the materials did not exhibit adequate physical and chemical properties. Another material developed by Dynatech, made of submicron glass fibers, was evaluated and tested, but it also proved to be unsatisfactory from a physical-properties standpoint.

Scheufelen Paper. It was noted in October 1968 that out of 33,000 different materials submitted to NASA, only 1 percent of them passed the 6.2 psia oxygen test conditions. Included in this 1 percent was a Scheufelen-developed cellulose-based paper which exhibited good flameproof properties, even at 16.5 psia/100 percent oxygen. In August 1968, 50 pages of two types of flameproof paper were sent to NASA, which, upon test, indicated a high probability of acceptance for the Apollo flight program. Numerous other samples and variations of these two original paper-like materials were made and sent to NASA; however, upon test results it was decided that this paper required additional improvement to satisfy the vacuum conditions likely to be encountered within the lunar module, on the lunar surface, or in an emergency command module decompression. The Scheufelen flameproof paper is basically a cellulose material, together with flame inhibitors and heat-sink mineral products with the additive of softeners and binders. Almost unlimited products can be imagined for this flameproof paper including wallpaper, napkins, tablecloths, clothing, toweling, facial tissues, toilet tissues, undergarment materials, foams, and other molded products. We have manufactured playing cards out of this paper for the astronauts' leisure time on the Skylab flights.

Paper Composites. Nonflammable paper composites have been produced having densities down to 5 percent of their apparent volume which exhibit exceptional physical properties. These composites have applications such as panels for aircraft, automobiles, and buildings.

Laminate Products. Laminates composed of one or more structural layers with a flameproof exterior layer have been produced. Since the structural layer can be made of very lightweight but structurally strong material, the laminated structure is not only strong but very light and flameproof.

Honeycomb Paper. Honeycomb panels are being produced out of flameproof paper by the Hexcel Corporation and the Koppers Company. These panels are made by cementing thin outer skins which are waterproof, nonflammable, and smooth surfaced over a honeycomb-paper inner layer. Again, it is very lightweight and nonflammable, and this material has many possible applications. We are particularly interested in its application for aircraft wall and ceiling panels; however, it would be equally applicable to automobile interiors, housing, and other such applications.

Papier-Maché Foam. In our search for a lightweight, inexpensive, nonflammable, and workable foam material, the Crew Systems Division conceived the idea of producing a fire-resistant paper foam which could be molded and shaped. They began an in-house developmental study of formulations and various processes and arrived at one which accomplished the desired results. This process consists of blending a wet paper pulp (made out of toilet tissue) with an elastomer binder and a fire-retardant chemical in a Waring blender, molding the mixture into various shapes, and drying the molds in an oven. Dried material resembles a foam material and is fireproof in 100 percent oxygen as well as being lightweight, inexpensive, easily obtainable, and workable. We are considering issuing a procurement to develop a process to additionally reduce the material density while maintaining its fireproof characteristics. Commercial production of this material is the prime effort of the successful awardee. Among the nonspace-oriented applications being considered are ceiling tiles, wallboard, fireproof packing and packaging material, acoustical material, etc.

Test Results. All of the materials discussed above were tested in our laboratories and proved to be nonflammable; however, the physical properties such as weight, density, toxicity, tear, puncture, abrasion, smoke, cleanability, light fastness, shrinkage, corrosion, and others must be considered when selecting a material for a particular application.

Conclusions. We feel that our nonflammable-materials-development program has proved to be highly successful and that we have improved the state of the art in nonflammable materials. Our goal, in addition to further development work, is to encourage the application of these materials in industry, military, public service, and domestic and institutional services.

1

## COMMERCIALIZATION OF NONFLAMMABLE PAPER TECHNOLOGY

Joseph A. Wray  
Battelle, Columbus Laboratories

Introduction. Mr. Radnofsky has presented some of the highlights of developments from the Manned Spacecraft Center on cellulosic nonflammable paper. He has also discussed and demonstrated some of the properties and possible uses of these products in the aerospace environment. The primary purpose of this paper is to extend the discussion a little further and suggest possible commercial application of this technology as a paper material or in related applications. Emphasis should be placed on related applications because in an initial review of the traditional paper markets there appears to be only limited application for this technology.

Traditional Paper Markets. The four major traditional market segments for paper and paperboard are illustrated in Table 1.

TABLE 1. TRADITIONAL PAPER MARKETS

<u>Printing and Publishing</u>	<u>Packaging</u>
<ul style="list-style-type: none"> <li>• Newspapers</li> <li>• Periodicals</li> <li>• Book Publishing</li> <li>• Commercial Printing</li> <li>• Manifold Business Forms</li> <li>• Stock Certificates, Currency</li> </ul>	<ul style="list-style-type: none"> <li>• Bags and Sacks</li> <li>• Corrugated Boxboard</li> <li>• Folding Cartons</li> <li>• Composite Cans</li> </ul>
<u>Construction</u>	<u>Sanitary Paper</u>
<ul style="list-style-type: none"> <li>• Roofing Paper</li> <li>• Wallboard</li> <li>• Ceiling Tile</li> </ul>	<ul style="list-style-type: none"> <li>• Facial and Toilet Tissue</li> <li>• Sanitary Napkins</li> <li>• Table Napkins and Towels</li> <li>• Disposable Diapers</li> </ul>

In the Printing and Publishing category, the use of nonflammable paper might have application in high-value paper uses such as stock certificates and currency. Also, some limited archival uses. In packaging, there is a potential market for nonflammable corrugated shipping containers that would be used to store goods in noninsured warehouses. The use of nonflammable paper for sanitary applications is not immediately obvious unless it is for use in commercial aviation and other specialty areas. The use of nonflammable paper in construction applications seems to have the greatest technical and economic feasibility.

Actually, the greatest overall potential for much of the technology developed at NASA is in product areas not related to traditional paper markets.

General Market Areas for Nonflammable Paper. Figure 1 graphically illustrates a number of general market areas for nonflammable paper technology. Emphasis is placed on the word, technology, since the technology is applicable to a wide variety of cellulosic substrates whether in the form of paper, textiles, or foam materials. The eventual transfer of NASA technology to commercial application will depend on a number of different factors.

Factors Affecting Nonflammable Material Use. Figure 2 illustrates a number of factors to be considered in the development of any commercial product. In the case of nonflammable products, one major factor is the legislative impact on product demand. The subject of government control brings to mind a number of generally accepted conclusions regarding fire protection.

- (1) The general population is not overly concerned with fire retardancy.
- (2) They will not generally pay extra for fire retardancy.
- (3) The major incentive for change to greater fire retardancy will come from legislative action.

Key Legislation Related to Nonflammable Products. Table 2 summarizes recent key legislative action related to flammability of materials.

TABLE 2. KEY LEGISLATION RELATED TO NONFLAMMABLE PRODUCTS

<u>Markets</u>	<u>Controlling Agency</u>	<u>Status of Regulation</u>	<u>Products Affected</u>
Aircraft	Dept. of Transportation	In effect Oct. 1968	All interior materials (fabric, foam, floor)
Automotive	Dept. of Transportation	Effective Sept. 1972	All interior materials
Carpets (>24 sq ft)	Dept. of Commerce	Std. in effect Apr. 1971	Natural and synthetic fibers, underlay, ...
Construction	Local and state governments	Building codes	All types
Children's Sleepwear	Dept. of Commerce	Effective July 1973	Sleepwear up to 6X (cotton-polyester, ...)
Hospitals and Nursing Homes	Dept. of H.E.W.	In effect	All interior materials of construction
Mattresses	Dept. of Commerce	Proposed and Published for Comment Fed. Reg. Sept. 1971	All mattresses (rubber, urethane foam, ...)

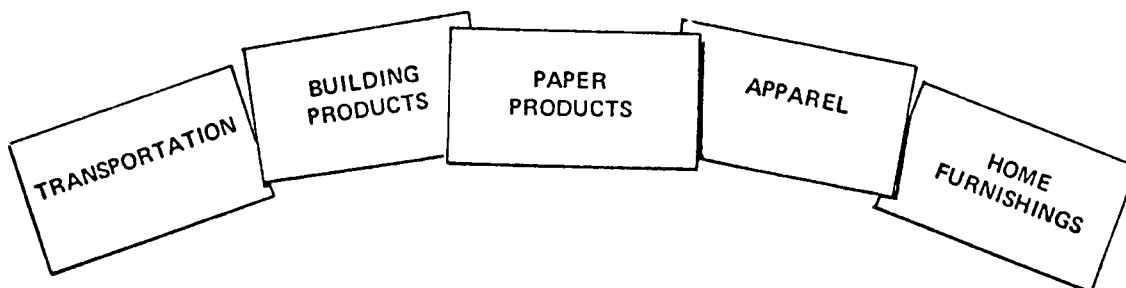


FIGURE 1. GENERAL MARKET AREAS FOR NONFLAMMABLE PAPER

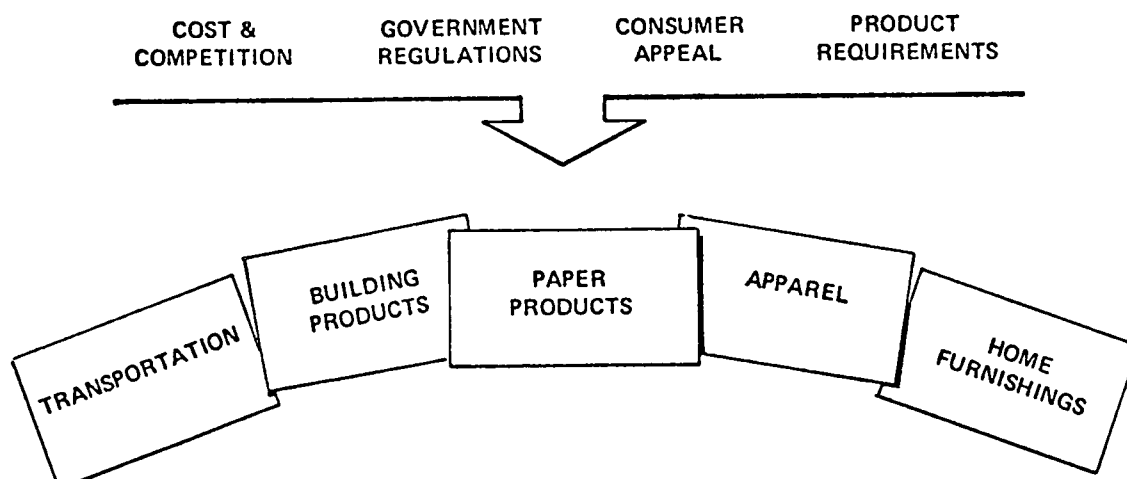


FIGURE 2. FACTORS AFFECTING NONFLAMMABLE MATERIAL USE

The chart covers a broad range of market areas including transportation, home furnishings, construction, and apparel. This chart was summarized and abstracted from the October 18, 1971, issue of Chemical and Engineering News. Probably one of the most significant pieces of legislation shown is the one covering children's sleepwear, Table 2 up to size 6X. In the October 1971 meeting of the Apparel Research Foundation, the child sleepwear bill was discussed in great detail and apparently is destined to cause many problems for both the textile and apparel manufacturer. It was mentioned during this meeting that the sleepwear bill would add about 30 percent to the cost of children's sleepwear. Initial enforcement of the children's sleepwear bill will begin in the summer of 1972 in that apparel that does not meet the standard will have to be labeled accordingly. Then in July 1973 those items not meeting the standard will be restricted from sale.

There is an interesting sidelight to the use of cellulosic materials in mattresses and upholstery. In a recent study conducted by Battelle's Columbus Laboratory for the Environmental Protection Agency, it was learned that large quantities of cotton mill waste that formerly were used as padding are now being discarded because of the increased use of foams and the burn characteristics of cellulose. This trend has added over 300 million pounds of textile fiber to the solid waste stream. The development of inexpensive non-flammable cotton waste product might help to minimize this problem.

Based on the discussion presented here, a number of product areas are suggested by this NASA technology.

Product Areas Suggested by NASA Technology. Some of these items presented in Table 3 are currently under investigation at NASA Manned Spacecraft Center in Houston and probably should be considered by industrial organizations for further commercialization. Automotive interiors include door panels, door and floor insulation, and headliners. The feasibility of developing cellulosic nonflammable foams has been demonstrated, but requires further development. In home furnishings, legislation is forcing the use of more and more nonflammable materials. In the apparel field in addition to children's sleepwear, there is other impending legislation that may eventually cover larger size children's sleepwear and possibly geriatric apparel for use in nursing homes.

Figures 3 and 4 illustrate some of the products described here that are currently being tested in NASA programs. Mr. Radnofsky may want to comment on these later during the question and answer period.

Technological Changes to Translate From Aerospace to Earth Environment. In the previous slides and discussion, we have talked primarily about marketing considerations in technology transfer. Some of the technical considerations are presented in Table 4. The three major research categories include

- (1) Material Combinations
- (2) Process Changes
- (3) Realistic Testing Procedures.

In some ways, the last item is perhaps the most important. Consideration has to be given to all aspects of flammability including rate and extent of flame spread, toxicity of fumes and smoke, and the rate of heat transfer and warning of fire that is provided the user.

TABLE 3. PRODUCT AREAS SUGGESTED BY NASA TECHNOLOGY

<u>Transportation</u>	<u>Building Products</u>
<ul style="list-style-type: none"> <li>• Aircraft Interiors (seats, flooring, overhead)</li> <li>• Automotive Interiors</li> <li>• Gaskets</li> <li>• Foams</li> </ul>	<ul style="list-style-type: none"> <li>• Ceiling and Wall Panels</li> <li>• Electrical Insulation</li> <li>• Wallboard</li> <li>• Wallpaper</li> </ul>
<u>Home Furnishings</u>	<u>Apparel</u>
<ul style="list-style-type: none"> <li>• Carpet and Backing</li> <li>• Floor Coverings</li> <li>• Furniture Upholstery</li> <li>• Mattress Covers</li> <li>• Drapes</li> </ul>	<ul style="list-style-type: none"> <li>• Foam Backings</li> <li>• Protective Clothing</li> <li>• Lab Coats</li> <li>• Sleepwear</li> <li>• Blankets</li> <li>• Geriatric Apparel</li> <li>• Operating Gowns and Supplies</li> <li>• Disposable Dresses, etc.</li> </ul>
<u>Paper Products</u>	
<ul style="list-style-type: none"> <li>• High Value (stocks, currency)</li> <li>• Printing</li> <li>• Packaging (unprotected warehouses)</li> </ul>	

In some limited work conducted by Battelle-Columbus and the Columbus Fire Department, the performance of various materials in actual fire situations has been studied. This work illustrated that the fire goes through a cyclic period and that the absence of oxygen and the presence of high levels of carbon monoxide and smoke are the major threats to life. Additional research of this type needs to be conducted using commercial and experimental materials.



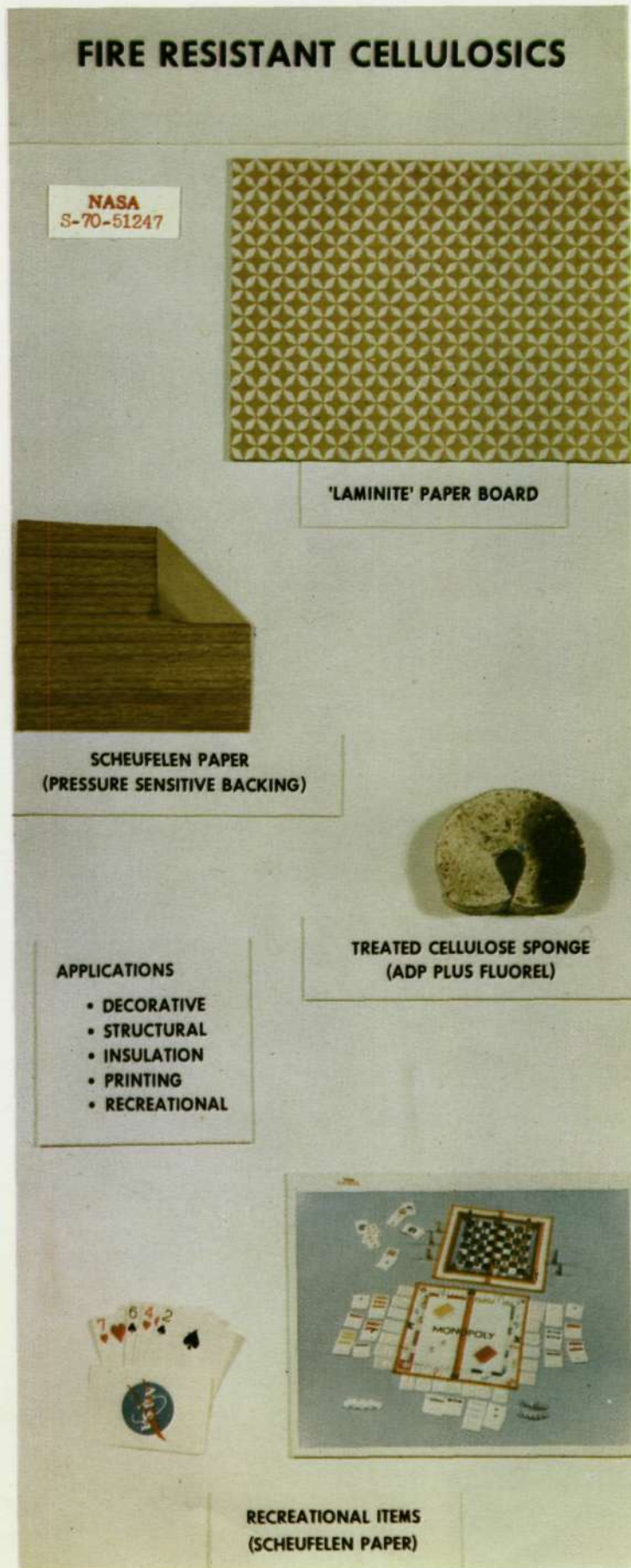


FIGURE 3. FIRE-RESISTANT  
CELLULOSICS DEVELOPED  
FOR AEROSPACE USE

NASA-S-71-1525-S

## NASA-2 GULFSTREAM

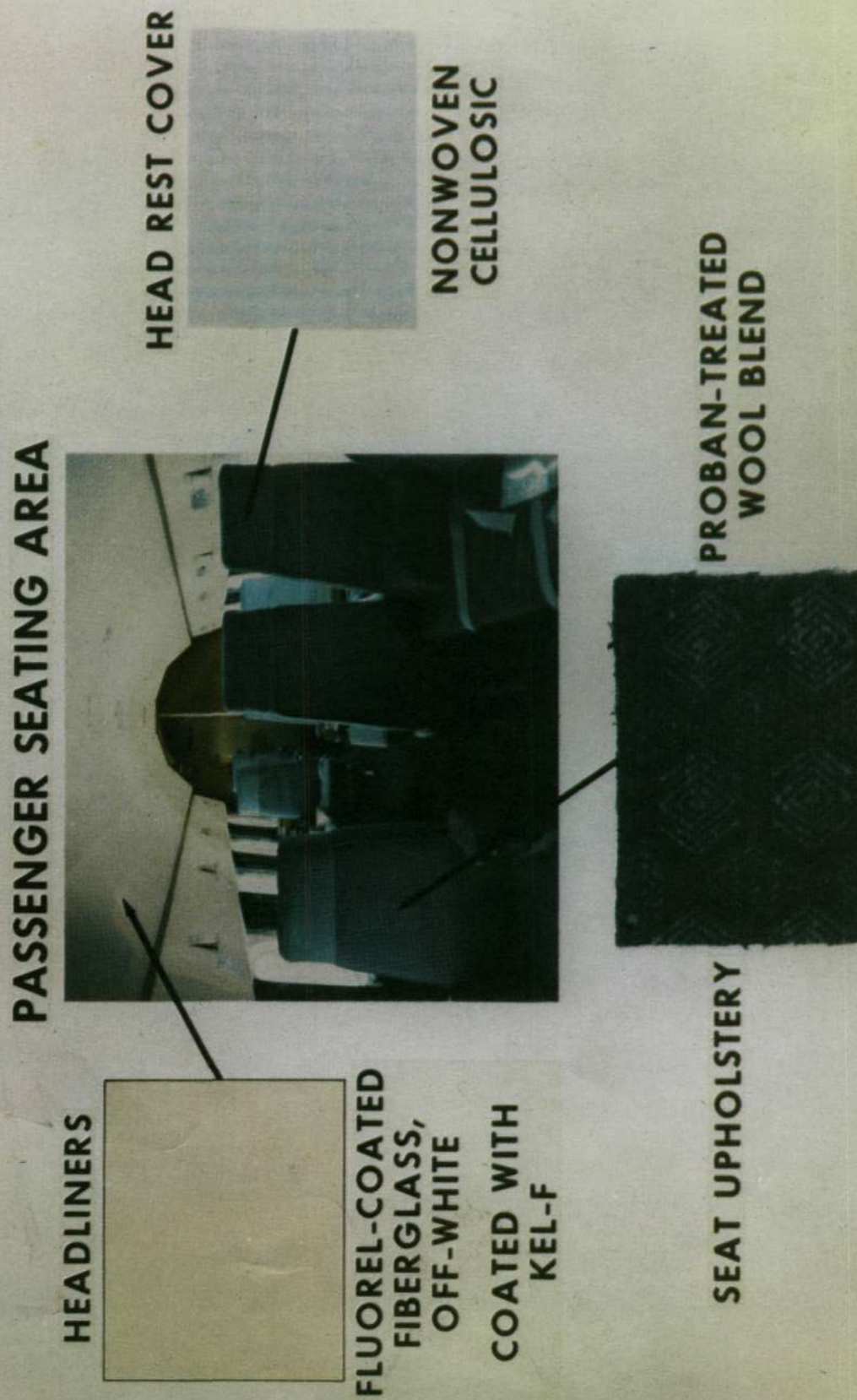


FIGURE 4. FIRE RESISTANT MATERIALS TESTED IN NASA AIRCRAFT

TABLE 4. TECHNOLOGICAL CHANGES TO TRANSLATE FROM  
AEROSPACE TO EARTH ENVIRONMENT

Material Combinations

- Fibers
- Surface Treatments
- Binders

Processing Changes

- Fiber Spinning to Expose  
Nonflammable Surface
- Nonwoven Technology -  
Wet Laid, Dry Laid, and  
Sandwich Constructions

Realistic Testing Procedures

- Flame Spread
- Toxicity
- Heat Transfer

## IMPROVED CIRCUIT BOARD LAMINATES

W. J. Patterson  
Marshall Space Flight Center

We had experienced a number of electronic component failures in various flight hardware, principally in the Saturn-Apollo program and some in subsequent programs of Marshall Space Flight Center. An alarming number of cracked solder connections were observed in the printed circuit boards of the electronic control assemblies. We have seen these in various ground support equipment and in flight hardware. Our tentative conclusion as to the failure mode was that the joints or the metal component leads were being either thermally or mechanically stressed beyond their capacity to absorb that stress. This led to an investigation of the expansion characteristics involved in the metallic and nonmetallic materials, as these various components and pieces of hardware were subjected to thermal cycling.

One of the standard MSFC printed circuit substrates is the G-10 epoxy fiberglass laminate. This is used fairly extensively in various hardware programs. If we consider the fairly wide difference in expansion coefficient of the epoxy materials and the metallic components in the printed circuits, then we can readily see how a possible failure mechanism would manifest itself when the circuitry was subjected to thermal stresses and thermal cycling. In Figure 1 is illustrated the general configuration that we are talking about. The printed circuit laminate substrate for the printed circuit is shown in this figure. It illustrates the cutaway view of the component mounted on the board, and the metal lead through the solder connection. The example further illustrates the type of hold board construction with a plated through hole and the various metallic interfaces.

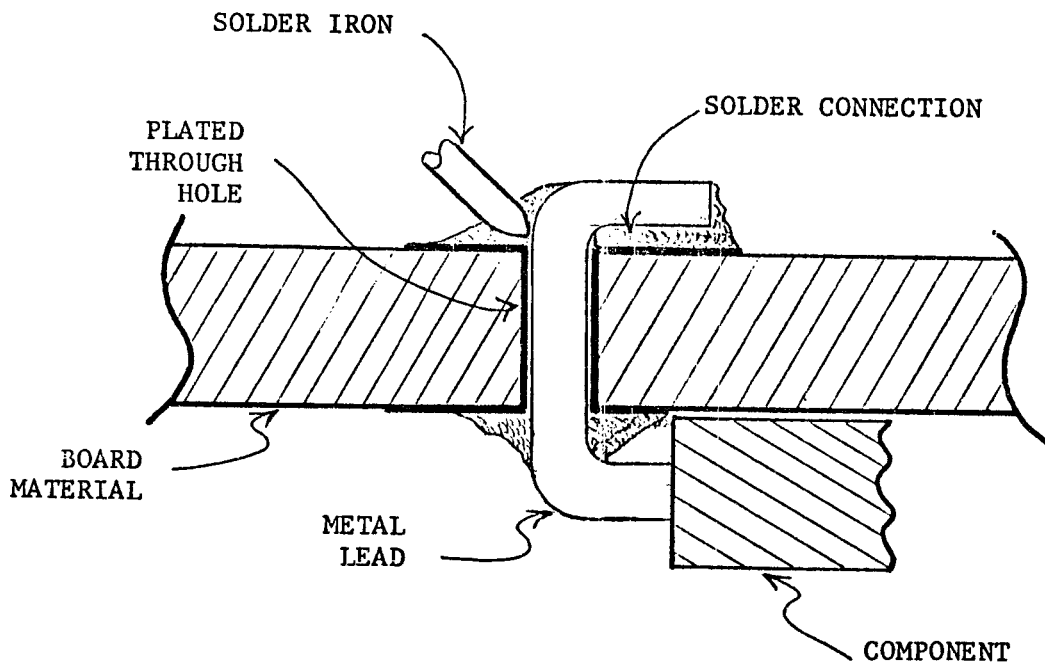


FIGURE 1. REPRESENTATIVE PRINTED CIRCUIT ASSEMBLY



The epoxy laminate, as is true with most laminates, is highly anisotropic with respect to the expansion coefficient. The coefficient of expansion is some three or four times as high along the axis normal to the plane of the board than in the plane of the board. This is due to the complete in-plane orientation of the glass reinforcement. As you can see from our configuration, the thickness axis is the critical dimension with respect to placing stresses on the solder joints. The component lead has an expansion coefficient of around  $15 \times 10^{-6}$  in./in./C, while that of the board is 60 to  $80 \times 10^{-6}$  in./in./C.

We feel the initial problem occurs in the fabrication of the joint itself. Let me point out that we are considering the configuration where the plated-through hole serves as the primary interconnect and the metal lead serves as a redundant path for the circuit to increase the reliability. As we begin the soldering operation--(the solder flows at about 650 F)--the heat is almost immediately transferred down through the length of the component lead into the metallic material comprising the plated-through hole walls, and we get an expansion of the metallic materials to the maximum extent for that particular temperature. Then as the process is continued, the heat tends to go out into the epoxy laminate which, if you recall, has a much higher expansion coefficient. The expansion tends to take place through the thickness plane. As the soldering operation is completed, the solder flows around the connection down through the hole until it is on the other side and begins to cool down. Thus the joint is essentially locked in this fully expanded position. The completed joint begins to cool down and we can see the possibility of residual stress in the joint. At elevated temperatures, the solder will deform plastically and relieve a certain amount of this stress, but it seems very likely that some residual stress is inescapably built into the joint. To compound the problem, most flight hardware is subjected to thermal cycling. If the joint is cooled below room temperature, the loading is going to increase tremendously and the stresses are going to increase accordingly. If the hardware is subjected to any thermal cycling either by way of testing in actual end use, we can see fatigue setting in the metal, and the repeated stressing can result in failure of the joint, as we have seen very often in our hardware. We feel that this is a result primarily of the residual stresses (either tensile or compressive) that are placed on the soldered joint in the plated-through holes due to this differential expansion coefficient of the component and substrate. Using the G-10 type epoxy laminate, this frequently occurs.

To give you a more vivid picture of the failures that we are talking about, I have included two figures that indicate two of the most common failure modes that are encountered in this type of hardware. Figure 2 shows a section through a soldered pad. The lead from the component has come through from the opposite side. The end of the lead is visible. The solder has been flowed around the end to make the connection. After thermal cycling, we begin to see this sort of failure pattern emerging--a circumferential crack all the way around. This may or may not disrupt the electrical continuity of the circuit, but it takes a pretty brave soul to fly hardware that looks like this. So we are not willing to take the chance.

The other type of failure mode that we see is a little bit more subtle, a little harder to uncover. In Figure 3 the sides of the wall of the hole going through the printed circuit board are shown. The component lead goes all the way through the thickness plane of the board, and the epoxy laminate

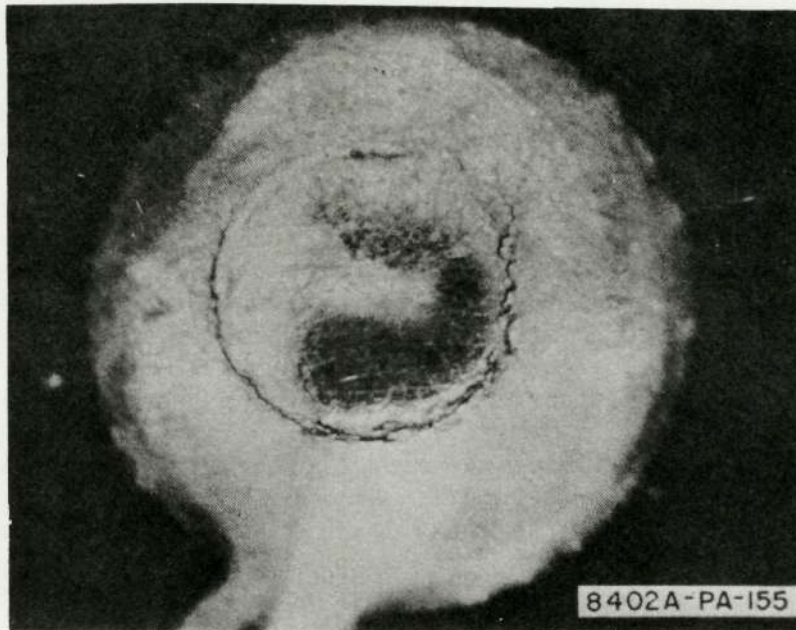


FIGURE 2. SOLDER JOINT

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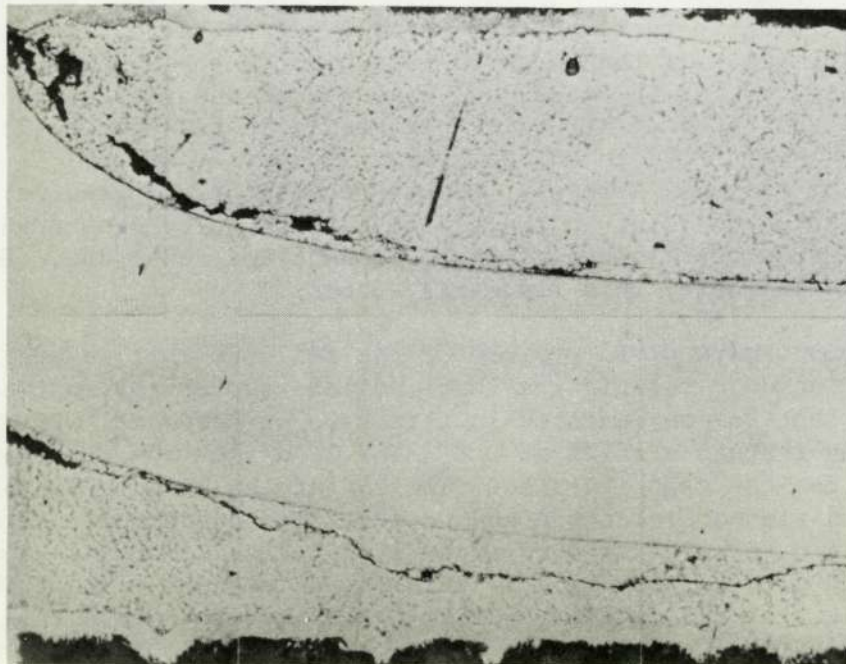


FIGURE 3 PLATED-THROUGH HOLE

is also visible. A thin film of metal is deposited to make the plated-through hole, and the solder fills the remaining void in the hole. You can see rather readily the cracking that was uncovered first by X-ray analysis in the micro-structure of the configuration.

Various solutions have been utilized to circumvent this problem. The most common have been the incorporation of stress-relief bends and of various types of spacers. These would absorb a certain amount of the stress brought on by the expansion of the board material and would prevent its transfer to the rather sensitive solder joint. However, these procedures do evade the basic issue, and they involve, as you can imagine, more costly and complicated fabrication procedures. Our preferred approach to the resolution of the problem was to reduce the inherent expansion of the board material in this critical thickness dimension to the point that it would approximate the expansion coefficient of the component lead material and the various metallic components in the joint. The material that we were primarily interested in and the one whose development was continued under the program has been a polyimide-based laminate. We initiated this development in the hope of optimizing the polyimide-glass composite to the point where we could match the expansion coefficients of the board and the metallic components and hopefully retain a processible laminate in terms of current printed-circuit-processing techniques.

A series of expansion coefficients for the various materials that go into the printed circuit assemblies are summarized in Table 1. The basic epoxy resin has a rather high expansion coefficient as you will notice. When you incorporate epoxies into a 30 percent-resin-content laminate, the overall coefficient of expansion is somewhat reduced, but it is still pretty high. The basic polyimide resin, as opposed to the epoxy, has an inherently lower expansion coefficient (around 50) and incorporated into the laminate the coefficient drops down further to 45. This inspired us to continue the development of the polyimide. It appeared that this was the most logical candidate for further optimization of the expansion properties. We still had quite a ways to go to approximate the coefficient of the metal component leads as you can see from the data in Table 1. The kovar seals that are often used in the circuitry exhibit even lower expansion than the leads. Obviously a considerable amount of optimization and various fabrication techniques had to be tried to reduce this thickness expansion. By the way, the values in Table 1 represent coefficients of expansion in the plane normal to the plane of the board, the dimension that we are most concerned with. The expansion in the plane of the board is quite low because practically all of the glass reinforcement is in this plane.

TABLE 1. EXPANSION OF CIRCUIT BOARD MATERIALS

Materials	Coefficient of Thermal Expansion $\times 10^6$ , in./in./C
Imide resin	50-55
Epoxy resin	80-100
30% imide laminate	45
30% epoxy laminate	61
Component leads	15-20
Kovar	6

One other advantage that we felt we would gain in going to the polyimide material is a higher glass transition temperature. Almost all of the epoxies have a glass transition point around 70 to 100 C. As the service temperature goes above the glass transition point, the expansion coefficient of the resin increases quite significantly, sometimes as much as doubling. In the polyimide material this situation does not arise in the service temperature range that we are concerned about. If the polyimide does have a true glass transition point, it is above the operating temperatures that we are concerned with. This further encouraged us to proceed with the optimization of the polyimide.

While the most urgent requirement of the program was the lowering of the expansion characteristics of the laminate, a series of other material requirements were also emerging. Several of these were antagonistic and required a certain amount of compromise or trade off as is so often the case. In Table 2 are outlined some of the more critical requirements that we imposed on the development program. Of course, the thickness expansion was the overriding objective. However, we were quite concerned about the other properties listed in the table. We were looking for a board that was thermally quite stable, one that would survive localized overheating of components without blistering, delaminating, or losing its dimensional stability. The polyimide board that Battelle subsequently worked on and developed has proved to be quite stable at the 200 C level. In fact, on thermal cycling back and forth from below room temperature to 200 C, we do not observe any delamination.

TABLE 2. CIRCUIT BOARD PROPERTY REQUIREMENTS

Thickness expansion	$15-20 \times 10^{-6}$
Thermal stability	Stable at 200 C
Flammability	Nonburning (oxygen-enriched environments)
Outgassing	$0.04\%/cm^2/hour$ , max at 200 C
Thermal conductivity	$15 \times 10^{-4} \text{ cal/sec/cm}^2/\text{cm/deg C/min}$
Processing	Equivalent to G-10 epoxy

Mr. Radnofsky has amply defined our problems in the area of flammability. We did want to build into the board as much fire-resistant character as we could. We knew that the polyimide laminates could be given a quite low order of flammability by deliberately resin-starving the board up to the point where they would pass the Marshall imposed flammability requirements (100 percent oxygen and 6.2 psi). However, this is only done at considerable sacrifice, in most cases, of the integrity of the board. Quite a bit of porous content and loss of mechanical properties are obtained. This was one of the compromises resolution of which may have to come where we are not concerned with a manned mission, where there is no hazard to astronauts' safety. Low outgassing properties were considered particularly important to missions such as the Apollo Telescope Mount (ATM). In that instance, we were very concerned with polymeric products in particular. Outgassed products in the hard space vacuum could subsequently redeposit on critical optical surfaces. The polyimide board is quite good in this respect. It certainly survives the Marshall requirements for the ATM. The composite performed quite well at 100 C and 200 C. The thermal conductivity of the board had to be as high as



possible to transfer heat efficiently away from components which might otherwise fail due to excessive heat generation. Mr. Bradbury, I think, will mention in some more detail the problems encountered with particulate fillers that we incorporated into the board.

Finally, we had hoped that the board would lend itself to current fabrication techniques. The sample of the doubly clad board being passed around among the audience is the fruit of Battelle's labors. It is a 1/16-inch-thick laminate, clad on both sides with 2-ounce copper. It has very amply satisfied our initial objectives of the thickness expansion characteristics, and for the most part it has met the other program requirements.

The board survives very well the thermal stability, coefficient of expansion, outgassing, and thermal conductivity tests. Some work has been done at Marshall subsequent to the Battelle effort with respect to processing studies, to see if the board will lend itself to current printed-circuit-fabrication techniques, or if we may have to modify these techniques substantially in order to take advantage of the very low thickness expansion of the board. The results of this preliminary test are reasonably good. The board that we have shown you lends itself to standard etching, soldering, and plating processes. I have brought along one of the circuit boards etched with a standard test pattern which Joe Bradbury will pass around. It indicates that the polyimide serves as a fairly good substrate for fabrication of the various circuit patterns. As I said, it etches, it survives the plating solutions reasonably well, and it solders reasonably well. There is no blistering or delamination at the higher temperatures. We deliberately took samples of the clad board and exposed it to isothermal aging in an air oven at 400, 500, and 600 F, respectively, and these will be passed around. I have a control sample along with the aged samples so that you can see for comparison how the integrity of the copper laminate interface was preserved. Even for 8 hours at 600 F, we did not see any blistering, or any significant delaminations that sometimes tend to plague the polyimide boards as a rule.

One of the problems which I should point out that we had encountered is in the drilling of the boards. The material is rather hard, and tends to have an abrasive effect when it is drilled. This is one of the areas that Marshall is currently working on and we feel that we can come up with alternate techniques to prepare the holes for circuit assembly.

5

## FURTHER DEVELOPMENTS AND COMMERCIAL PRODUCTION

Elmer J. Bradbury  
Battelle, Columbus Laboratories

Jerry Patterson has defined the need at NASA and Palmer Stickney stole a little bit of my thunder; I'm going to describe some of the interreacting properties that we had to work with, some of the problems that we encountered, and the solutions that we came up with. Since NASA does have a very exacting combination of requirements, this was a complex system and we will have to start from that premise.

I would like to show in Table 1 the general approach used at BCL on this problem. First of all, we attempted to delineate the major task requirements and relate these to the board construction. Jerry has gone into this in fair length and discussed the task targets and pertinent reasons, so I won't belabor the requirements. I will, however, speak about the relevant factors of construction and composites. This will serve as a foundation for our projection of methods for improving the composite properties. There were a number of interreacting methods and systems used in this program. These will be reviewed briefly and I will discuss the fabrication of this system from the standpoint of conventional circuit board manufacture and techniques. Finally, I will attempt a projection of areas wherein this particular system might be useful and where one might modify the system, change processing techniques or materials, to extend the applicability of this system's concept.

TABLE 1. DEVELOPMENT PHILOSOPHY

- I Definition of Task Requirements
- II Establishment of Relevant Factors
- III Methods for Improving Composite Properties
- IV Fabrication of Improved System

Jerry has introduced the circuit board for you to examine and I would like to discuss circuit board construction in general. As shown in Figure 1 there are copper foils on either side. You have an adhesive layer and there is a substrate. The substrate can be comprised of a number of different reinforcing fabrics. Depending upon the laminate thickness needed, this may have anywhere from four layers of 182 cloth up to 24 layers of 112 fabric. Thus, depending upon the number of plies of fabric used you may have anywhere from 6 to something like 25 resin interfaces or resin layers in the laminate. Jerry has introduced the fact that much of their work was done with the G-10 type system. The G-10, the G-11, FR-4, and FR-5 are all epoxy-based systems. These use various resin modifications and generally the same type of construction.

## TYPICAL CIRCUIT BOARD CONSTRUCTION

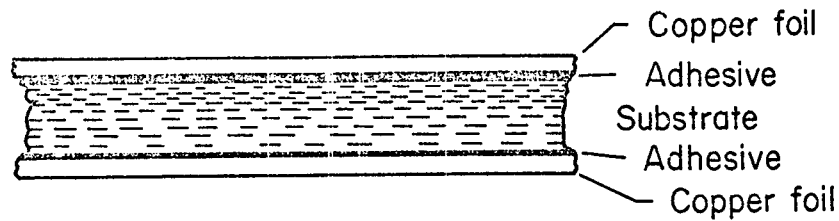


FIGURE 1. TYPICAL CIRCUIT BOARD CONSTRUCTION

- G-10 - General purpose epoxy system
- G-11 - Better elevated temperature properties than G-10
- FR-4 - Flame-resistant epoxy similar in properties to G-10
- FR-5 - Flame-resistant epoxy similar in properties to G-11

Jerry has pointed out that the major problem was the expansion in the thickness direction in Figure 1. I would like now to dig into the problem, to determine how great the magnitude of the problem is and to project the approaches to solution. We have in Figure 2 a graphical representation of the expansion coefficients of (1) the glass reinforcement, (2) the copper facing, and (3) the epoxy binder used in a G-10 type board. The open portion of the bars in Figure 2 represents the general range of expansion behavior. The bottom two bars represent circuit board expansion. The longitudinal bar shows the in-plane behavior of the circuit board; and the bottom bar shows the expansion normal to the circuit board. This is quite significantly larger than copper. The longitudinal expansion is a little less than copper. With a proper balance of resin and reinforcement the longitudinal or in-place expansion can be fairly close to copper. Generally speaking, most circuit boards are designed to provide that balance.

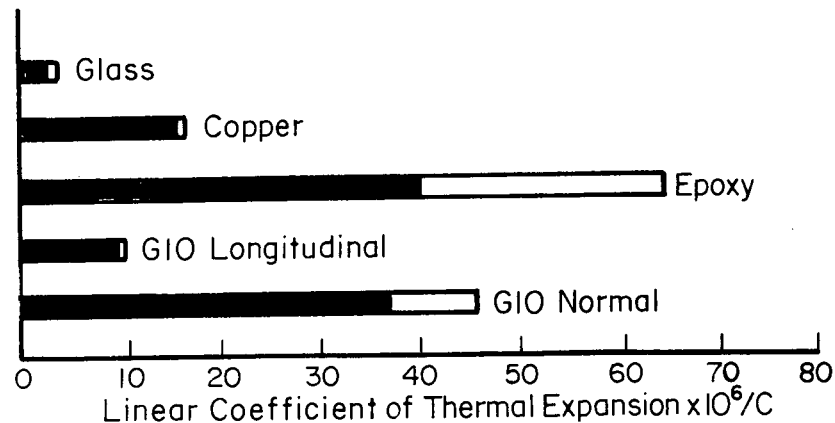


FIGURE 2. THERMAL-EXPANSION CHARACTERISTICS OF CIRCUIT BOARD CONSTITUENTS

The construction of glass fiber reinforcements is shown in Table 2. Styles 7628 and 1528 are used fairly widely in conventional circuit boards. These styles are medium weight fabrics. This means that either 8 or 9 plies will be required for a 1/16-inch nominal laminate. Depending upon the number of plies used, the resin content may vary slightly around 35 percent. Style 112 is a much lighter fabric, such that 24 to 25 plies are required in a 1/16-inch nominal laminate. This obviously means a lot of handwork. Style 182 is a much heavier fabric requiring about 4 plies for a 1/16-inch laminate.

The HS-1 style fabric is a tridirectional reinforcement that subsequently was used in the development as a means of controlling part of the Z-direction expansion. The Z-direction of course is normal to the plane of the board.

Since the expansion problem primarily is related to the resin, I would like to discuss the resin-filler interrelationship. Figure 3 shows the relationship between epoxy and glass based on the rule of mixtures. In general, the rule of mixtures states that the expansion or the thermal conductivity is a linear relationship between the volume ratios of the two materials. Figure 3 relates several expansion values for epoxy with various glass contents. The nominal G-10 composition is designated on this figure to show that the G-10 composition does, in fact, have a considerably larger expansion than can be tolerated. Further, this does not show the effect of anisotropy which Jerry mentioned previously. This means that the confining action of the reinforcement on the resin will result in a larger expansion in the normal direction. As was shown previously, this expansion of the circuit board will fall in the region of 35 to 45 in./in./C which is, of course, larger than the normal rule of mixtures.

Another factor which Jerry made reference to is that of glass transition. I would like to show how this relates to the problem. Figure 4 shows the expansion of a laminate normal to the plane of the board. The board has a rather low expansion coefficient below 75 C. However, when you reach the glass transition you'll note that the expansion rises very abruptly. So that even if one were to match the coefficient of expansion normal to the plane of the board to that of copper for the lower temperature range, once the glass transition temperature is exceeded the expansion would exert tremendous loading on soldered connections. The solution to the expansion problem accordingly is intimately related to glass transition behavior. Suffice it to say, we checked a number of different methods, used a number of different resins in an attempt to raise the glass transition above 200 C. While we did get some nominal improvement with the epoxy systems, none of the approaches showed a glass transition above 200, such that the epoxy could be used then as the basic binder for the desired improved circuit board. This, of course, forced consideration of the use of high temperature resins.

Jerry has shown some of the properties of the polyimides. Table 3 shows the property range for various molded polyimides and polyamide-imides. The coefficient of linear expansion is somewhat less than that of epoxy resins. Specific gravity is about the same. The heat distortion is considerably above that of epoxies and gives an idea of the high temperature capability of these resins. So the transition temperature would be expected to be somewhat above the target temperature of 200. Thermal conductivity is to all intents and purposes very similar to that of the epoxies. Water

TABLE 2. CONSTRUCTION CHARACTERISTICS OF GLASS FABRIC REINFORCEMENT

Style	Construction W x F	(a)		(b)		Filament Diameter, in.	Thickness, in.	Weight, oz/sq yd	Tensile	
		Warp	Fill	Yarn					W x F, lb/in.	Weave
7628	42 x 32	75-1/0	75-1/0			0.00036	0.0070	5.80	225 x 200	Plain
1528	42 x 32	150-1/2	150-1/2			0.00036	0.0070	5.95	250 x 200	Plain
112	40 x 39	450-1/2	450-1/2			0.00021	0.0032	2.10	82 x 80	Plain
182	60 x 56	225-2/2	225-2/2			0.00029	0.0135	12.60	550 x 450	8 Sh. Satin

(a) The number of warp and fill ends per inch of fabric.

(b) First number relates to yarn strand count, namely, the approximate yardage per pound of strand in hundreds of yards; e.g., 75 indicates an approximate strand length of 7500 yards per pound. The second series of numbers designate the number of plies in the yarn. The first digit tells the number of single strands twisted. The second digit, separated from the first digit by a diagonal line, designates the number of strands plied together. The total number of strands are obtained by multiplying these two numbers (0 is multiplied as one).

Fabric Style	Weight, oz/sq yd	Lengthwise						Crosswise			Vertical	
		Ground			Stuffer			Filament			Filament	
		Percent Total	Filament Diameter, mils	Filament Diameter, mils	Percent Total	Filament Diameter, mils	Filament Diameter, mils	Percent Total	Filament Diameter, mils	Percent Total	Filament Diameter, mils	Filament Diameter, mils
HS-1	15.0	50	0.25	0.25	5	0.25	0.25	24	0.25	21	0.21	0.21

TABLE 3. PROPERTIES OF HIGH-TEMPERATURE RESINS

Test	ASTM No.	Units	Commercial Molded AI/Polyimides (a)
Shore D Hardness	-	-	92
Barcol Hardness	-	-	50
Coefficient of Linear Thermal Expansion	D-696	in./in./C	$34-54 \times 10^{-6}$ (23 C - 200 C)
Specific Gravity	D-792	-	1.40-1.43
Heat Distortion	D-648	C	280-360
Thermal Conductivity	-	-	1.1-3.3
Water Absorption 24 hours	D-570	percent	0.21-0.32
Fire Resistance	D-635	-	

(a) Values reported in manufacturers' literature.

absorption is about the same. Fire resistance tends to be somewhat better than that of the epoxy system. However, with the anticipated use of filler and the fact that reinforcement is required, this then we felt would improve the fire resistance of the resin and the nonburning characteristics of the circuit board.

In summary then, we needed an insulating high temperature binder; one that had low expansion; one that probably would have to be reinforced in order to obtain the physical properties; and one in which reinforcement would not significantly affect the expansion behavior so that we could in truth have the same expansion both normal and in the plane of the board. From the standpoint of using a modified epoxy or epoxy-based resin we felt that this would not solve the problem because of the  $T_g$ . As far as finding one with an exceedingly low expansion, other resins have about the same expansion behavior as the epoxy. Finally, the thermal stability requirements necessitated the consideration of polyimides.

With the other approach to control of the expansion through the use of a smaller amount of resin conceivably one could hold the expansion down. Jerry has alluded to this from the standpoint of flammability. If the resin content is reduced to approximately 50 percent, expansion is controlled. However, you now have resin starvation as a factor and other properties of the laminate suffer. We felt that we could not tolerate this. The question thus was, how could we effectively use somewhat less resin to achieve the type of expansion control needed? We felt that a solution to this could be to use a filler in the resin such that the matrix would have sufficient flow characteristics. This system

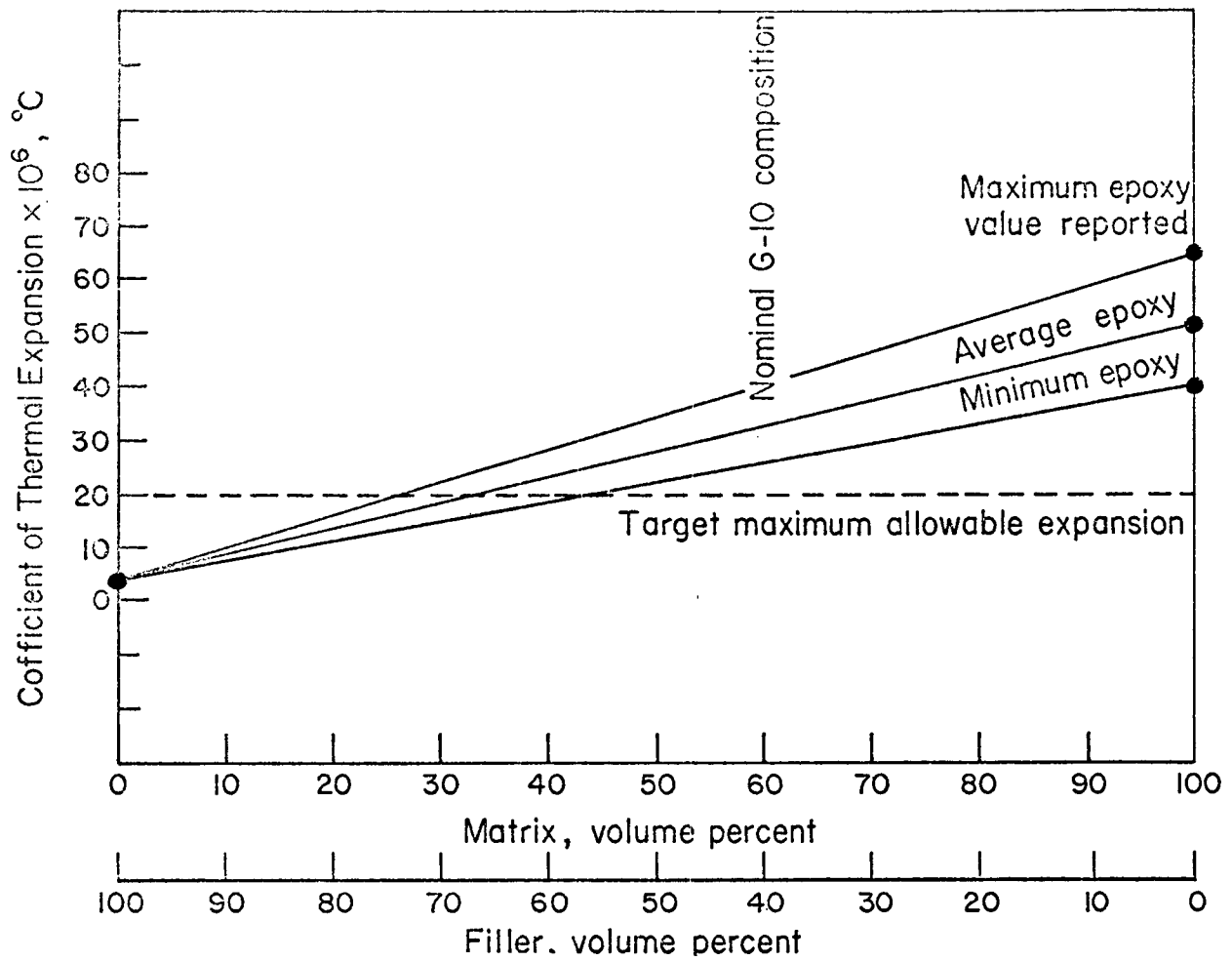


FIGURE 3. GENERAL CORRELATION OF COMPOSITE COMPOSITION WITH THERMAL EXPANSION CHARACTERISTICS

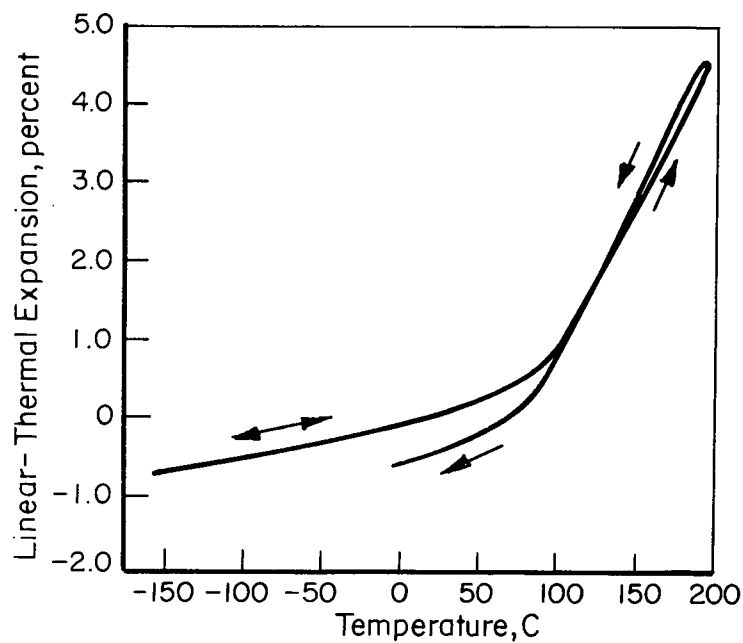


FIGURE 4. LINEAR-THERMAL EXPANSION OF LAMINATE NO. 26127-14 (NORMAL)

then would be a matrix capable of thermal expansion control. From the standpoint of flexural capabilities, we felt that we needed a matrix; this would be resin plus filler of around 35 weight percent, since this has been shown to have approximately optimum flexural properties.

With this background in rationale, we will take a quick look at the generalized filler properties in Table 4. Glass, of course, has a relatively low thermal conductivity; and thermal expansion as you can see is quite low. Minerals have an even lower thermal conductivity; thermal expansion is about the same as glass. Refractories -- we do have an indication that we have something which will have some conductivity properties. Jerry has indicated the desirability of heat conductivity in this circuit board. In refractory materials we do have a thermal expansion which runs the gamut from a negative expansion with temperature up to a very high thermal expansion. Finally, Table 4 shows a miscellaneous category where materials have good thermal conductivities and modest thermal expansions. The miscellaneous category includes graphite which we considered from the standpoint of conductivity but then had to discard because this also tends to be electrically conductive. This accordingly is unsuitable for circuit board use. We also considered tungsten carbide, and, in fact, this does conduct heat very well, but Jerry has alluded to the drilling problem. We felt that with tungsten carbide filler fabrication difficulties would be untenable. We anticipated some difficulties with alumina but hoped that we could live with alumina filler machinery problems.

TABLE 4. GENERALIZED FILLER PROPERTIES

Material	Specific Gravity	Thermal Conductivity, g-cal/sec/cm <sup>2</sup> /C/cm	Thermal Expansion, in./in./C x 10 <sup>6</sup>
Glasses	2.5-2.6	0.001 to 0.003	2.8 to 6.0
Minerals	2.5-3.1	0.0001 to 0.0003	2 to 6
Refractories	2.6-5.5	0.001 to 0.15	-0.4 to 139
Miscellaneous	1.8-3.2	0.001 to 0.4	0.5 to 7.2

Preliminary studies with alumina in the G-10 epoxy system indicated that hydrated alumina would give a fairly satisfactory result. However, when we attempted to use a polyimide matrix we found other problems. The high processing temperature resulted in a very porous type material. Originally, we thought possibly that the porosity was due to the polyimide processing. Accordingly, we used DTA, and a TGA-mass spectrometer train to determine the outgassing and to establish optimum processing conditions for the polyimide resin. However, even under highly controlled conditions, we still found problems. Ultimately by running a TGA-mass spectrometer analysis on the filler we found that the hydrated filler was breaking down under the processing conditions. With this background then we were able to project the use of alumina in polyimides.



The hydrate-induced porosity was estimated by using a hard fired alumina, ball milled in order to get the fine particle size needed. We still had porosity problems with some of the polyimides, but about this point in time a resin P13N became available. I will not go into the chemistry or the processing because Ernie Boller later in the program will discuss these at some length. Suffice it to say that this resin did work in very nicely with the background previously obtained. We found that the concept of limited loading with this resin was quite satisfactory. We now were able to achieve the proper trade-off in the expansion characteristics and in the conductivity. Earlier in this paper the fact was discussed that woven fabric tended to give a high degree of restraint in the in-plane direction. It also was shown that in the normal direction expansion was actually accentuated or aggravated by virtue of the fact that it could not expand in plane. With this in mind we felt that we should not adjust the matrix properties to the point where it matched that of copper. In this event, the in-plane restraint would cause the in-plane expansion to be too small and as a result shear stresses would develop between the copper and the substrate. To counteract this then, we went to the HS-1 fabric which was shown earlier. During the course of our work we came up with the construction shown in Figure 5. This shows the general construction of the laminate faced on both sides with electrolytic copper foil. The 7628 fabrics were used as an outer facing on the core to control the surface finish. The layers of HS-1 fabric were used primarily for control of Z-direction expansion but these did contribute to laminate properties. I would like now to discuss in more depth some of the problems attendant with this development. Early work with the standard type of copper foil revealed that we had a problem with the service capability. The high processing temperature did give good bonding and good peel, but ultimately when an attempt was made to use the board it was found that during the processing sequence the bond strength was lost in the gold plating bath. We reasoned that during the processing of this laminate the temperature was sufficiently high to cause oxidation on the reticular surface of the copper foil. This is a very pure copper, and very highly reactive. Consequently, it doesn't take very long at high temperature to produce a film of copper oxide which is soluble in the cyanide containing bath. Accordingly, we found that protection was needed for the copper bonding surface. Otherwise, during the steps of the manufacture of the circuitry, the exposure to the cyanide solutions would result in the dissolution of copper oxide and loss of all integrity so far as the copper foil and substrate were concerned. A source of electrolytic copper coated with nickel to act as a protective surface was found. The nickel can be processed similarly to copper and is not subject to oxidation under the same conditions as the copper. We then developed the matrix. It was found that 22.5 volume percent of filler in the matrix would provide the behavior we wanted with respect to thermal expansion. We found also that the HS-1 which has about 21 percent of fiber in the vertical direction would satisfactorily restrain the Z-direction expansion. Rotating the HS-1 90 degrees with each ply produced a reasonably well-balanced laminate. The 7628 fabric was used as a facing primarily to control the surface finish. However, it is a balanced fabric and does contribute to good flexural properties.

Another aspect in this development is the use of proper coupling agents. These, of course, are quite critical in providing the integrity in the overall construction and enhancing compatibility of the compounds. This then comprises the NASA circuit board.

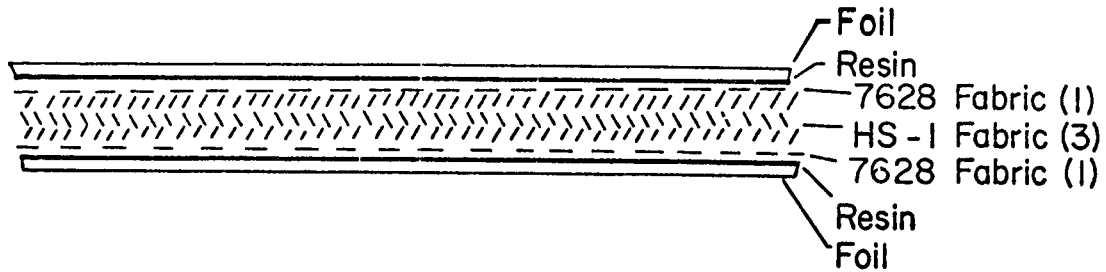


FIGURE 5. NASA DEVELOPED CIRCUIT BOARD SYSTEM

## Materials Specifications:

- (1) Nickel - coated copper
- (2) Matrix 22.5 v/o filler
- (3) Prepreg 35 w/o matrix
- (4) Reinforcements sequenced 90° each ply.

The question consistent with the aims of this program was "Where do we go from here?". I would like now to think in terms of utility, modification, and processing concepts as shown in Table 5. Utility, of course, will refer to the circuit board such as we have developed. This relates primarily to the dimensional stability, thermal stability, expansion control and the dielectric characteristics of the board. Obviously this has a good potential for areas where these characteristics are required. Modification, of course, would relate to areas wherein the board might be changed to cut down on the relative cost of the product to accommodate the mass market. Processing relates to the conventional and other methods for heating and fabricating the composite.

TABLE 5. UMP PROJECTION

## Utility

Dimensional Stability  
 Thermal Stability  
 Thermal Expansion Control  
 Dielectric

## Modification

Resin  
 Reinforcement  
 Fillers

## Processing

Conventional  
 Inductive  
 Microwave

So far as modification is concerned, any resin which has a  $T_g$  which will be higher than the normal range of projected operations could be used. For example, the Hystl resin which was discussed this morning might achieve a balance of properties which would be compatible with various systems operating below the  $T_g$ . Reinforcement, if strength is a requirement, undoubtedly will require a woven type reinforcement. Glass is usually considered, but it does not necessarily have to be glass, depending upon the a priori projected service. The reinforcement could be graphite, asbestos, or new generation fibers. Reinforcement selection, of course, will depend on whether the target is for electrical applications.

There is another aspect of reinforcing that I would like to insert here and that is the possibility of interspersing metal fibers or metal filaments in a glass-reinforced system. I will discuss possibilities of this type of hybrid system a little later in relation to processing potential.

There are any number of fillers that can be considered that will be less expensive and less difficult to machine than the alumina which we utilized to meet the targets of this development. Glass, of course, is readily available and inexpensive, and does have many desirable properties. If expansion control is the primary target, glass could be used as a substitute for alumina. This would eliminate one of the problem areas of the circuit board developed for NASA, that of machining. Parenthetically, I might say that limited work with lasers has indicated that this might be a suitable method for drilling such a reinforced filled system.

In summary then, if the service temperature requirement can be relaxed lower cost resins can be used. These generally will simplify the processing and the fabrication cost and still give acceptable properties. The use of less expensive and abrasive fillers will establish a trade-off in the expansion control and machining. Such fillers still will give a balance of properties that can be used in critical nonspace applications. Fabrics, graphite, asbestos, or metal combined with a foam filler, for example, might give low-density, high-strength composites for critical nonspace motor applications. The system developed for NASA needed a high-temperature resin and as a consequence high-temperature press capabilities were necessary for the fabrication. If a lower temperature resin can be used, then obviously conventional equipment can be used.

Processing of a composite such as has been discussed generally requires heat and pressure. It does not follow, however, that the heat must be obtained by using thermal sources. I would like to suggest the possibility of using microwave, dielectric or induction heating. Induction heating would lend itself very nicely to the use of metal reinforcement or hybrid systems such as were suggested previously. This could be in the form of either sheet forming compounds, or bulk molding compounds. The use of either inductive or microwave heating which will couple to uncured resins and to polar type compounds also would allow for quick heat-up within the thickness of the composite. Through heating by any of these methods, followed by a press cycle, could very quickly produce a formed composite. Conversely, the normal fabrication utilizing heat from a thermal source is limited by the rate that the heat can be transferred from the surface. High surface temperatures required for fast heat-up will tend to cure the surface before the entire composite is ready to form.

I would like now to discuss very briefly areas such as are shown in Table 6 in which this particular type composite or new generation composites developed from this might be used. Obviously we are talking in terms of such items as electrical circuit boards, electronic components and switch components. an advanced concept I would like to suggest at this time is the use of a metal or a metal complex filler which can be reduced. This could form the basis for an additive type process where the reduced metal filler becomes a catalyst for deposition of copper or a similar conductor not only on the surface but also in the holes through the circuit board. Another area in which the use of a filled composite with controlled thermal expansion is that requiring electroplating. As was shown during discussion of this development, the expansion of the circuit board based on the unfilled system was considerably greater than that of copper. Obviously, then heated, unfilled resins will expand greater than the electroplate or metal coating on it. Judicious use of fillers and reinforcements would be expected to improve the service behavior of such systems.

TABLE 6. POTENTIAL AREAS FOR UTILIZATION

Electrical
Circuit boards
Electronic components
Appliance
Equipment
Housing
Structural
Air conditioning
Automotive
Marine

Another area in which the use of filler-reinforcement concepts might be valuable is the structural type laminates, and decorative laminates where warp is a considerable problem. The use of expansion control concepts in those could eliminate or minimize that aspect of difficulty.

In summary then, I believe that there is considerable potential for circuit boards, both conventional and additive, decorative laminates, industrial laminates, electrical control systems, all relating to the use of stable, complex, expansion-controlled systems such as we have been discussing here.

# PROFIT OPPORTUNITIES FOR IMPROVED POLYIMIDE RESINS

Ernest R. Boller  
Applications Manager, Applied Technology Division  
TRW Systems Group, Redondo Beach, California

Polyimide technology has been a basis of chemical product activity at TRW for several years. Our discussion of profit opportunities for polyimide resins will be concerned with the original development of the materials, and the product commercialization efforts which TRW then embarked upon. We will also review the status of this polyimide technology today.

A chronological flow of the polyimide technology over the time period 1964 to 1971 is shown in Figure 1. The NASA and Air Force contracts undertaken by TRW are shown as well as the company-sponsored programs. This discussion will deal primarily with the ablative resin contracts (NAS 3-4188 and NAS 3-7949) and the commercial development, market introduction, and market development of the A-type polyimides. Market development is currently being accomplished by Ciba-Geigy Corporation under a license from TRW. The current NASA and Air Force contracts which are concerned with A-type technology in application to adhesives, laminates, and autoclave composite are also indicated in Figure 1 and will be briefly reviewed later.

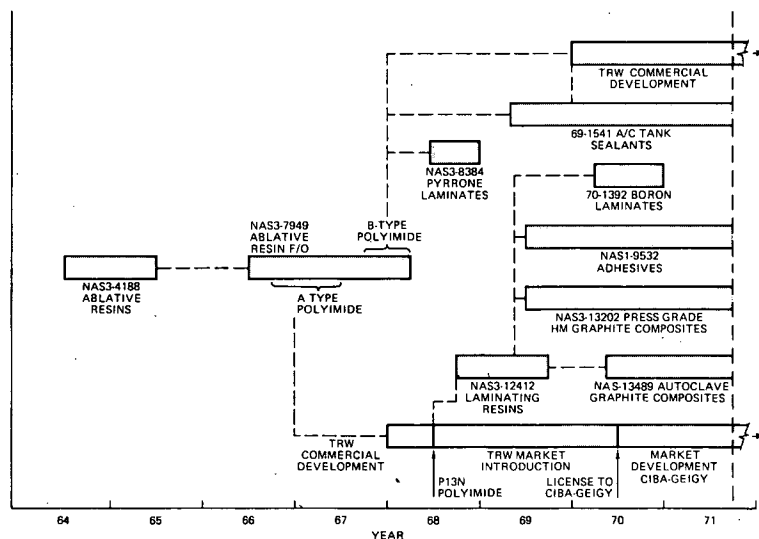


FIGURE 1. IMPROVED POLYIMIDE RESINS CHRONOLOGICAL FLOW OF TECHNOLOGY

The term "A-type Polyimides" refers to a family of polyimides which cure through an addition reaction rather than a condensation reaction. To put it another way, the imidization occurs separately and apart from the cure. The ramification is that low-void composites are easily obtained. The A-type polyimides consist chemically of aromatic dianhydrides and aromatic diamines in combination with nadic anhydride. The P13N specifically is composed of benzophenone tetracarboxylic acid dianhydride (BTDA), methylene dianiline (MDA), and nadic anhydride (NA).

The top portion of Figure 1 depicts a separate sequence of technology which is labeled "B-type Polyimides". This technology has its origin in the ablative resin contracts also and has been the subject of commercial development at TRW. This technology will not be discussed today, but it is shown to indicate the total chronological flow of polyimide technology at TRW.

The contracts which TRW Systems undertook for NASA/Lewis Research Center during the period 1964 through 1967 (Table 1) had as their objective the evaluation of resin matrix materials for ablative applications. Specifically, the application was in propulsion systems which utilized fluorine-containing propellants. The objective was to evaluate not only existing materials but to develop criteria for the selection of new polymer systems for this particular application. The criteria which were established are listed in Table 1. The ease of processing was important. At that time, in 1965 and 1966, all high-temperature aromatic resins that were commercially available were cured through condensation. We concentrated on the aromatic resins because they did give a char residue which had structural integrity. This was important in the ablative application. The structure and the chemistry of cure as related to the criteria were considered. We intentionally attempted to devise polymer configurations which, while possessing the thermal and mechanical properties of aromatic materials at high temperature, were easily processed. Some of the polymer families considered were boron polymer systems, silicone-containing polymers, polybenzimidazoles, and polyimides.

TABLE 1. INITIAL NASA CONTRACTS

(NAS 3-4188 and NAS 3-7949)

Objective: Evaluate and prepare ablative resin matrices suitable for use under conditions imposed by fluorine-containing propellants

Criteria for Selection of Resins:

- Thermal and oxidative stability
- Low thermal conductivity
- Resistance to erosion
- Low molecular weight pyrolysis gases
- Dimensional stability of char residue
- Ease of processing

The A-type polyimides, the composition of matter of which was filed as a disclosure under these particular NASA contracts, gave very good retention of properties at 550 F. They gave good char stability and were very easily processed. Extended postcuring fabrication cycles were not required. Thermal conductivity and resistance to erosion were influenced by choice of reinforcement rather than resin. These materials were exposed to fluorine propellant torch tests within the laboratory. These tests simulated the conditions imposed by a rocket engine exhaust on an ablative material. On the basis of these particular tests, the polyimide systems were well suited for the ablative application. The objectives of the contract were met. Upon completion of the evaluation of ablative resin systems, two rocket nozzle inserts were fabricated: one from A-type polyimide with glass reinforcement; the other with graphite reinforcement (Figure 2). These two inserts were shipped to NASA for their evaluation in test engines.

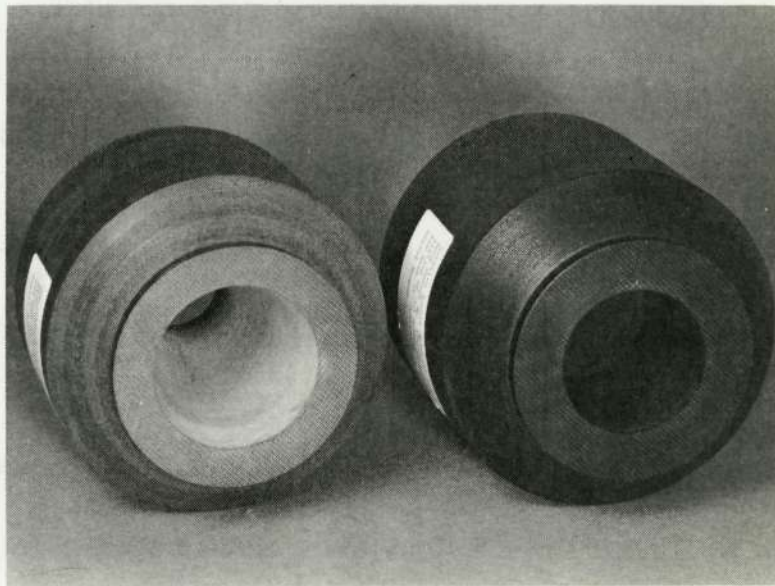


FIGURE 2. ROCKET NOZZLE INSERTS FABRICATED FROM REINFORCED A-TYPE POLYIMIDE

Another example of an A-type polyimide application is shown in Figure 3. This is a polyimide/glass laminate as removed from a press. It turns out that there are many structural composite applications which have the same problems of fabrication that were investigated on the NASA contracts specifically for ablative inserts and liners for rocket engines. Therefore, TRW considered commercial development of the technology. Criteria for selection of chemical products for commercial development at TRW are listed in Table 2. Good patent protection is required at TRW before commercial development is considered.



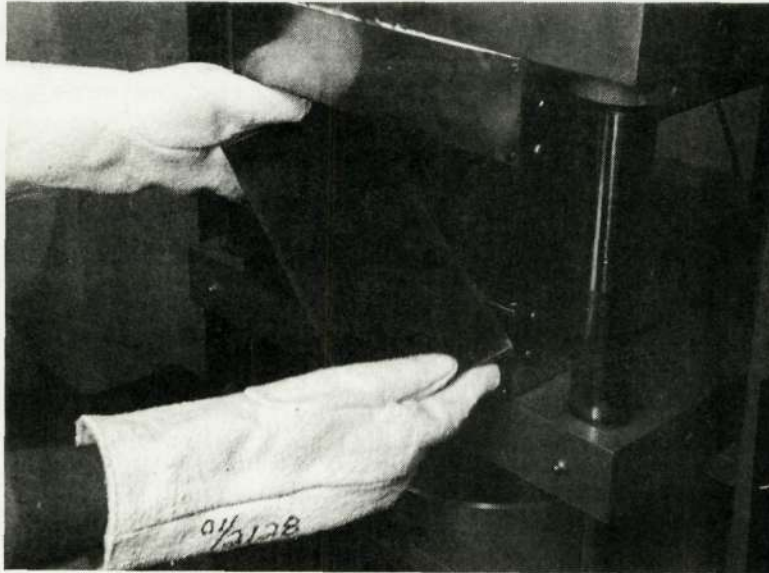


FIGURE 3. A-TYPE POLYIMIDE/GLASS LAMINATE

TABLE 2. CRITERIA FOR SELECTION OF CHEMICAL PRODUCTS  
FOR COMMERCIAL DEVELOPMENT AT TRW

- Commercial merit based equally on technical performance and price
- Some principal uses in technical/market areas at TRW systems
- Aerospace market application
- Product form must be suitable for evaluation by many customers
- Can be manufactured by TRW using articles of commerce

As shown at the top of the list, the value of the product had to be based on both performance and price. TRW Systems as an aerospace company is not in a position to compete with large chemical manufacturing concerns on strictly a price basis. The products must be able to stand on their superior technical performance and properties.

At this point a definition of "commercial development" is in order. It is the making available of products for numerous aerospace and other industrial applications through the use of company discretionary funding.

A second criterion for selection was that some of the principle uses of the material must be in technical/market areas at TRW. This is to permit a rapid internal assessment of a product. For example, a prime product line at TRW is the manufacture of jet engine components. One potential application polyimide resins is in jet engine components. In this case we were able to make rapid assessment of the product (polyimide) performance potential.



Third, the products had to have aerospace market application. The reason is that TRW knows the aerospace market well. Commercial success must be based on a thoroughly understood market.

Fourth, the product form must be suitable for evaluation by many customers. The product form must lend to quick evaluation by many customers with a variety of end uses.

And finally, can it be manufactured by TRW using articles of commerce? The raw materials must be commercially available. The A-type polyimides did meet all of these criteria. TRW requested a commercial waiver from NASA and embarked upon commercial development.

At the end of this commercial development period, which took place during 1968, a specific product based upon the A-type technology had been defined. P13N Press Grade Laminating Varnish was introduced in 1968. It is a polyimide; it is sold as an imide acid in DMF. The features of this material are shown in Table 3. The low void content is easily obtained because the cure is accomplished through addition rather than condensation; the water of condensation is removed before cure begins. It is the combination of low void content with rapid processing that made P13N a very interesting and exciting product in 1968 and for that matter today. Depending on the thickness of the component cure times can be as short as 1 hour. Extended post cure is not necessary. The prepreg is stable at room temperature for extended periods of time. Composites employing P13N maintained excellent long term mechanical properties at temperature. Low void content is the main reason for maintenance of properties.

TABLE 3. FEATURES OF COMPOSITE PRODUCTS UTILIZING  
P13N PRESS-GRADE LAMINATING VARNISH

- Low void content
- Rapid processing
- Stable pre-preg
- Excellent mechanical strength
- Long term thermal stability

Properties of the P13N are shown in Table 4 for both the neat polymer and with various reinforcements. Of particular interest is the interlaminar shear of graphite-reinforced P13N at both room temperature and 550 F.

The initial end-use markets which were identified for the P13N Press Grade Laminating Varnish are listed in Table 5. With reference to the previously stated criteria for a commercial chemical product at TRW, these end markets are of interest to TRW and afforded opportunity for internal evaluation. Glass/polyimide composites find aerospace application as radomes, graphite/polyimide composites as jet engine components, and boron/polyimide composites as structural panels and members.

Market introduction of the P13N is outlined in Table 6. First, the necessary sales and process bulletins were prepared. As with most specialty products, a large amount of application information was developed for the P13N.

TABLE 4. PROPERTIES OF P13N POLYIMIDE RESIN

	<u>Cured Polymer</u>	<u>Glass Laminate (a)</u>	<u>Graphite Laminate (b)</u>	<u>Boron Laminate (c)</u>
Tensile strength at 73 F, psi	11,000			
Tensile modulus at 73 F, psi	550,000			
Elongation, percent	2.5			
Flexural strength, 10 <sup>3</sup> psi				
at 73 F		91.2	254	283
at 550 F		69.6	201	198
Flexural modulus, 10 <sup>6</sup> psi				
at 73 F		3.5	20.1	32.4
at 550 F		3.1	15.5	25.8
Interlaminar shear, 10 <sup>3</sup> psi				
at 73 F		9.0	16.3	11.5
at 550 F		6.5	15.5	5.8

(a) 1/8-inch-thick laminate, 75.5 percent Style 181 glass cloth.

(b) 1/8-inch-thick laminate, 65 percent "Morganite II" fiber (polyacrylonitrile precursor).

(c) 1/8-inch-thick laminate, 60 percent boron fiber.

TABLE 5. END USE - MARKETS FOR P13N  
POLYIMIDE RESIN

- Missile and supersonic aircraft glass composite components
- Jet engine graphite composite components
- Aircraft structural boron composites

TABLE 6. MARKET INTRODUCTION OF P13N  
POLYIMIDE RESIN

- Technical service - process bulletins and calls
- Dissemination of sales brochures
- Trade magazine announcements
- Technical society exhibits

These data consisted of prepreg preparation suggestions, imidization and cure cycles, storage data on the material and physical property information. We introduced the P13N at a price of \$105/gallon. No sampling was done except in very special cases. At this introductory price it was assumed that very few product developers would purchase unless they had a serious and immediate need for the P13N. It was a way of screening customer inquiries with a minimum of effort.

The price has been reduced several times since introduction. The current price schedule from Ciba-Geigy in 55 gallon quantities is \$25 per gallon or about \$7.50 per pound of contained resin. Papers were presented and products exhibited at various SAMPE and SPI meetings. Short notices appeared in the trade journals. Over an 18-month period, there were over 70 customers for the material. P13N was the resin chosen after competitive evaluation on the Advanced Composite Engine program undertaken by Pratt and Whitney under AFML contract.

It became apparent during the introduction of the P13N into these aerospace applications that there were other markets for various product forms based on the technology. Remember that P13N is only a press grade laminating varnish for composite fabrication. An autoclave varnish, that is a material which possessed satisfactory flow properties for autoclave fabrication, was required for more complex geometries. There were various friction and wear applications which could utilize a molding compound based upon this high-temperature resin system. And there were applications for high-temperature adhesives, particularly in the case of bonding a composite structure to a metal structure. TRW did not have and does not have the marketing and sales organization necessary to move a broad line of chemicals, particularly in non-aerospace markets. If this technology was to find its way into these broader end-use markets, this type of organization was necessary. Ciba-Geigy has an outstanding reputation in the specialty chemical product business, and has a broadly experienced marketing group. They received a world-wide exclusive license from TRW in 1970 for the P13N technology and are currently the supplier of this product.

TRW involvement, however, continues. In addition to working with Ciba-Geigy, we are involved with several government contracts which impact the technology. These contracts are shown in Figure 1 and pertain to specific requirements which NASA and Air Force have for boron reinforced composites, press and autoclave graphite composites and high-temperature adhesives. Several of the products and their applications are indicated in Table 7. The P13N is the only material which is commercially available at this point in time. Several of the others are approaching the point of commercial availability. The products shown cover a range of applications and in some cases provide higher temperature properties than does the P13N depending on the application.

In summary, the P13N polyimide has been successfully moved from product origin under a NASA contract to full commercial status as a chemical product. The applications have been broadly extended beyond the original ablative resin application. But the effort does not stop here. Continuing development will assure maximum utility of the technology.

TABLE 7. PRODUCTS BASED ON A-TYPE POLYIMIDE TECHNOLOGY

<u>Polyimide</u>	<u>Applications</u>	<u>Development Contract</u>
P13N	Press molding for ~550 F service	NAS 3-7949 and TRW Commercial
P10P	Press molding for ~600 F service	NAS 3-13489
P10PA	Autoclave molding for ~600 F service	NAS 3-13489
P105A	Autoclave molding for ~550 F service	F33615-70C-1392
P11B	Press bonding for ~600 F service	NAS 1-9532
P11BA	Autoclave bonding and molding for ~600 F service	NAS 1-9532

## POSSIBLE FURTHER DEVELOPMENTS

William R. Dunnavant  
Battelle, Columbus Laboratories

Man-made polymers have now been tailored to meet the requirements of an incredibly large number of end-use applications. As has been commented earlier, plastics are highly prized engineering materials because of their unique properties or combinations of properties. Unfortunately, all of these valuable properties can easily be destroyed by heat at temperatures at which products are sometimes expected to perform. It hasn't been too many years ago that resistance to boiling water was the mark of a high-temperature polymer. We've come a long way since that time. In recent years we have seen intense efforts to develop plastics suitable for use at temperatures as high as 300 C or higher. While some of these materials can perform only briefly at elevated temperatures, others have proven capable of functioning for long periods of time, and in doing so protect life, sensitive electronic components, or various delicate substrates from intense heat.

By necessity a number of NASA-supported research programs have been directed toward the development of more heat-resistant polymeric materials. The program carried out by TRW and just described by Mr. Boller represents one of these efforts. In addition, I think it represents a most important milestone in high-temperature polymer technology. Such milestones are important and worth your consideration because each prior one in the particular field has led to the advent of significant new products and profit opportunities for industry.

The present and future potentials of the pyrolytic polymerization products developed by TRW and Ciba-Geigy can perhaps best be appreciated by just briefly considering certain of the technical advances that occurred earlier. To demonstrate useful properties at elevated temperatures a polymer chain must generally do two things. It must remain intact and it must retain some degree of rigidity. Most conventional thermoplastics such as polystyrene, PVC and polyethylene soften or melt at temperatures well below their decomposition temperatures. This means that their maximum service temperatures tend to fall far below their actual decomposition temperatures. Various methods have been used for increasing the rigidities of such polymers. These have included the production of crystalline modifications. This work, for example, has resulted in higher heat deflection temperature forms of polyethylene and polypropylene. The attachment of certain polar groups to carbon chains has also been used to advantage. Success with this approach is evidenced by the higher decomposition temperature and service temperature achieved with polyperfluoroethylene.

Cross-linking, or the tying together of polymer chains by suitable connecting linkages, has long provided one of the simplest and most effective ways to raise the service temperature ceilings of thermoplastics. This approach is perhaps best demonstrated, however, in the properties of materials in the thermoset class, which includes such materials as the epoxies, phenolics and silicone resins. Here again, the upper temperature limits of these polymer types are time dependent, as they are in all cases with polymers.

For many years resins of the thermoset types have been relied upon in applications where unusually high heat resistance was required. Each of the earlier approaches for raising service temperature ceilings has provided numerous opportunities for industry in the form of new products and markets. In most cases the products obtained had other valuable and salable properties in addition to improved heat resistance. However, the properties of materials of these types were not sufficient to meet all the requirements posed by military, aerospace, and industrial needs.

In the 1960's a new generation of polymers arose having significantly increased thermal decomposition temperatures. These materials were achieved by incorporating highly stable aromatic or heterocyclic rings directly into the polymer chains. As in the case of organic polymers in general an infinite variety of such polymers is potentially available and is limited only by the availability and cost of the building blocks. This effort to develop inherently rigid polymer chains led to two separate classes of new materials. The first of these is a group of high heat deflection temperature thermoplastics which includes the polycarbonates, polyphenylene oxides, polysulfones, and polyphenylene sulfides. These polymers, in general, can be fabricated with more or less conventional or slightly modified polymer processing equipment and are finding permanent places in the marketplace for applications not only requiring heat resistance, but high impact strength, good electrical properties, and generally outstanding mechanical properties.

The second group of materials contain still more stable but appreciably more difficult to fabricate materials, such as the polyimides, polybenzimidazoles, incideamides, and the Pyrone materials. The Pyrone group of materials, of course, is another example of a polymer system that was developed under NASA programs and represents one of the more thermal oxidatively stable, as well as radiation resistant, systems that are currently available. As has been noted earlier, only a few examples of this second group of materials have reached the market place to date. But the impact of the polyimides and polyimide-amides, for example, in the electrical insulation and composite areas is well known. Several of these polymers have now been to the moon and back. They have played vital roles in making those historic trips possible.

In their final form the aromatic-heterocyclic group of polymers are largely infusible and insoluble, properties which make their fabrication difficult or in some cases impossible. Fortunately, some of them can be prepared in novel two-step processes in which soluble, high-molecular weight prepolymers are obtained having reactive pendant groups. The rigid, stable rings in the final polymers are formed by thermally induced condensations of the reactive groups pendant to the polymer chains. As Mr. Boller has pointed out, virtually all of the aromatic-heterocyclic polymers available to date cure by this particular mechanism with the net result that substantial quantities of water are evolved during the processes. This evolution of water is difficult to handle during a fabrication process. The prepolymers are, thus, of types that are subject to moisture-induced degradation and require careful storage and handling.

The conversion of the usual aromatic-heterocyclic polymers into fibers or films or for use as composite binders depends largely on the solubilities of their prepolymers. Because the conversion of the prepolymers to the final heat-resistant structures involve the evolution of a substantial quantities of water, the use of such materials is limited largely to the formation of coatings, films, fibers and other applications in which effective volatile

release can be accomplished. Thus, the production of high-quality plastic parts of such size as to require substantial volatile release distances, such as a thick composite, has not proven to be very satisfactory.

In view of the limitations of these earlier polymer systems, the pyrolytic polymerization work described by Mr. Boller will have to be recognized as a most significant breakthrough in polymer technology. For the first time, polymeric materials having truly high-temperature capabilities, together with ease of fabrication approaching those of more conventional thermoset or thermoplastic type materials, are available. Let's consider for a moment several of the requirements that a practical heat-resistant polymer should have. It should have high molecular weight in order to provide good mechanical and useful engineering properties. This is achieved in the P13N system during the curing process. The polymer should contain stable, rigidizing links and stable connective links. The P13N system meets both of these requirements. The polymer must be formable at some stage in its development. In this particular case the P13N system has a double advantage. It can be fabricated both from solution, and the thermoplastic properties of its low-molecular weight precursor can be taken advantage of. Last, but not least, the polymer must have technologically useful properties at the intended service temperature. I think that Mr. Boller's earlier talk has amply borne out the fact that the P13N system has this capability. All things considered, it seems likely that the pyrolytic polymerization products meet these requirements better than any earlier materials. They are capable of doing most anything that earlier polymer systems were capable of doing and more. The new polymers are unique in that unlike other maximum stability systems, the final forms of the polymers are arrived at through the use of relatively small and soluble precursor molecules. Of perhaps more importance, however, is the fact that the final desired polymer structure is arrived at without volatiles being evolved. Therefore, the previous serious problem of volatile and void formation during fabrication is avoided. The curing mechanism is also important in that cures of the resin can be achieved significantly more rapidly than with earlier systems. In general, the mechanics of using resins of this type should not prove alien to fabricators having experience with the conventional thermoset type resins and considerably less art should be required in fabricating high-temperature components. This factor will in turn provide a higher degree of reproducibility in production processes and again help to reduce production costs.

The inherently rigid chain polymer systems developed during the last decade have frequently been termed the new generation polymers. The advent of pyrolytic polymerization products will probably give birth to an equally large class of new polymers and one, I think, that will prove to be equally, if not more, important from a commercial standpoint. Many chemical modifications of the present P13N type system will arise. Some of these materials are and will be made by Mr. Boller's group and by Ciba-Geigy. Others will be developed by other organizations, perhaps some of those represented here today. Much of the earlier high-temperature polymer technology will be applied in expanding the pyrolytic polymerization concept. A wide variety of stable ring systems other than those containing imide groups can be inserted between reactive end groups such as those used in P13N. We will no doubt see systems containing not only imide but perhaps benzimidazole, Pyrone and other stable groups in second generation products. Many of these materials I'm sure are being made and evaluated at the present time. It would not be surprising to see some polymers evolve containing less exotic ring systems, such as aromatic polyamide units, for example, for use in more moderate temperature applications.

A variety of copolymers containing more than one type of stable ring system can also be visualized. Block polymers in which two or more types of pyrolytic polymerization systems are co-reacted might warrant attention. Mixed polymers of some of these resins could conceivably provide unique properties for specific applications. These properties might include, for example, especially high thermal oxidative resistance, resistance to specific corrosive chemicals, or to meet unusual dimensional stability problems.

In addition to polymers containing other than imide linkages, we can expect to see similar types of polymers having new types of addition polymerizable end groups. Some of these new end groups have already been identified and the resulting new polymers are being developed. Certain of these new materials may combine ready fabricability with even higher use-temperature ceilings as a consequence of these improved end groups and the connecting linkages that they subsequently provide in the cured polymers.

Heat resistance in a polymer is a property that commands a premium. The relatively small amounts of materials required in most end-use applications often does not preclude the use of premium priced resins. Nevertheless, reduction in resin costs are desirable and will no doubt occur. The raw materials from which most truly high-temperature polymers are prepared have been relatively difficult to produce and purify in the past. Improved preparative methods for certain of these intermediates will no doubt be achieved. It will ultimately provide high-temperature performance at a more reduced cost. The development of new procedures for preparing the required intermediates was largely ignored until recent years, but is now receiving increased attention on the part of NASA, other Government agencies, and industry.

The availability of these new stable and processable polyimides should provide a wealth of opportunities, not only for resin manufacturers, but for plastic product designers and engineers, fabricators, raw materials suppliers and others. It is apparent that, from a fabricating standpoint, the new polyimides can be considered for use in many manufacturing processes in which the solubility and thermoplastic properties of the prepolymers can be taken advantage of.

Many applications have already been cited here today for the PI3N materials such as adhesives, coatings, ablators, supersonic aircraft components, circuit boards, electrical wire and cable insulation, and a wide variety of molded items including self-lubricating bearings, valve seats, and so forth. In addition to the more usual processes for fabricating new polymers into useful end products, perhaps more consideration should be given to the use of some of the more unusual fabricating techniques that might be employed. For example, do the unique properties of the new polyimides suggest novel products or solutions to problems that might be realized through the use of fluidized bed coating or plasma spray coating techniques? What would be the potential advantages of making certain polyimide-based parts by isostatic or explosive forming processes? Do the new polymers provide some unique advantages with respect to filament wound structures?

Many industrial organizations deal with one or more products or processes in which a heat-resistant polymer might advantageously replace a less effective material now in use. It is relatively easy to find reasons for replacing one polymer with a better one. However, some of the more interesting and unique applications of polymers will result from the replacement of a nonpolymeric



material for a given job. For example, where are glass, ceramic or metals now being used to do a job that a heat-resistant polymer might do better?

Another potentially enormous market for plastic materials has been touched on here today a number of times. This is to use the material not alone but in conjunction with other materials. Not only is the use of all types of fibre reinforced plastics growing by leaps and bounds, but plastics filled with virtually all conceivable types of organic and inorganic materials are finding unique applications.

It might be well to point out in closing that the new polyimides, as is the case with other high-temperature polymers, could provide solutions to many problems in which heat resistance is not the major concern. To consider the opposite extreme, they might provide an answer for a problem involving cryogenic conditions. Could it be that they have surface characteristics that would make them invaluable in a variety of medical applications, or in the general field of membrane technology? Is there a place for these new polyimides in the area of flame retardant textiles? Here is a case in which, I think, we can be reasonably certain that there will be major R&D efforts made in the future, the impetus being provided by an increasingly safety conscious public and by actions taken by various legislative bodies.

Thus, future developments regarding new polyimides are likely to include such things as the development of more stable connecting linkages, lower cost precursors, the development of novel fabricating techniques, and the development of new end use applications. A new class of polymeric materials always presents a challenge to a number of sectors of the plastics industry. Where we go from here seems limited only by our imaginations.

## INTUMESCENT COATINGS (RESUMÉ)

John A. Parker  
NASA Ames Research Center  
Moffett Field, California

NASA Ames Research Center has developed a new intumescent technology from a continuing study which is applying the principles of thermochemistry to polymeric materials. Military applications have been the primary target and many applications are now operational. However, several commercial, non-military end-uses have also been uncovered.

The overall program can be divided into three areas - (1) foam technology as generated from spacecraft studies, (2) the extension of this foam technology into a new intumescent coating technology, and (3) the successful combination of these two technologies to protect aircraft. The objectives of aircraft protection are improved crash-fire survivability along with ballistic survivability as may be required to defeat an incendiary projectile in a combat situation. This general type of information is directly applicable to the generation of new products which are useful in blocking the heat generated by all types of fires (e.g., household, fuel). It was found that low-density polymethane foams possessed good thermochemical properties because they were excellent radiative ablators with low heating rates. Materials with specific activation temperatures have been prepared by suspending fire suppressants in microballoons. A major processing achievement was obtained by combining mineral fibers such as glass or quartz with the low-density foams to obtain improved mechanical properties, i.e., physical strength at very low density.

Durable coating systems described in some detail in the following talk have also been produced which function not only as points but also generate low-density fire-resistant foams under the influence of heat. These coating systems have now been refined to the point where they possess excellent rates and general weather resistances.

Today, both foam and coating technologies are being combined in an effort to obtain passenger protection in commercial aircraft. Tomorrow, NASA-Ames looks to a basic improvement in the efficiency of the foam to further insure survivability. This program will include the study of new window materials to resist the intrusion of fire, bulkheads to act as complete fire barriers, and significant biological animal testing for toxicity.

## FURTHER DEVELOPMENTS AND COMMERCIAL PRODUCTION

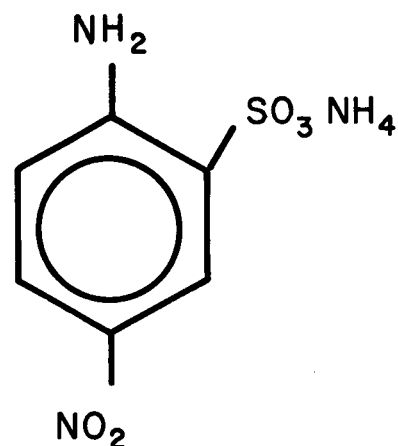
Richard J. Dick  
Battelle, Columbus Laboratories

Introduction. We have been meeting here today to discuss technological transfer, specifically, in an attempt to align NASA material applications with the commercial (industrial) market. In outlining some of the problems and plusses of applying space technology (in this case, intumescence) with the business community, we should focus mainly on the determination of the commercialization potential of these materials.

To acquaint you with the potential of the intumescent coatings developed through the efforts of Ames Research Center, I will comment briefly on the development, the technology, several applications, and the market development aspects of their ongoing program. First, it must be emphasized that we are only talking about one compound - the ammonium salt of paranitroaniline ortho-sulfonic acid (Figure 1). The performance of this material is radically different from that in any other existing intumescent system. Although Ames has examined, and continues to examine, a wide variety of materials as intumescent agents, the ammonium salt of p-nitroaniline is the intumescent agent we are discussing today.

FIGURE 1.

AMMONIUM SALT OF  
PARA-NITROANILINE  
SULFONIC ACID



As we all know, intumescence generally is achieved by including unreactive inorganic compounds of low molecular weight to induce a char in gas-forming reactions; very classically, the use of the acid phosphates. However, low molecular weight materials leave the final product easily water-extractable and this is highly undesirable from the standpoint of weathering. Quite contrary to this, the ammonium salt of p-nitroaniline is relatively water insoluble and is also easy to seal in the resin binder when formulated into a coating.

It is important for you to be acquainted with the basic forms in which Ames offers this intumescent chemistry.

- (1) The basic formulation (Table 1) illustrates the incorporation of the ammonium salt into an epoxy-polysulfide resin system. This produces a coating with excellent weathering and intumescent qualities. However, when this material was applied to bombs, it was found that it lacked adhesion and would shrink and do some strange things on cylindrical surfaces because of the nature of the intumescent process.
- (2) Ames discovered very quickly that the addition of small amounts of chopped glass fibers ( $\pm 25\%$ ) resolved this problem and this modification was coded #313.
- (3) The third adventure in the intumescent agent's form was a linoleum similar to a leathery sheet. This sheet has tremendous flexibility and the material is used as a wrapping material.
- (4) The fourth generation of this family incorporates a long fiber material. This can be chopped and sprayed with a chopping and spraying gun simultaneously to yield better insulation and better application to large tanks, as used for propane-butane storage situations.
- (5) A new (fifth) generation material which I'm sure you've not yet heard about is the availability of this material in rod, cruciform, and various shapes. For example, if you wish to fill up a room it would be unnecessary to coat the room or hang it with drapes; just use three or four rods of this material which, when temperature-activated, would react and fill the room. This is a void filling control concept.
- (6) Still another concept uses a sack of intumescent material which is hung in a void area. Obviously, this approach requires no application technique and lends itself well to situations requiring frequent inspections.

To get a feeling for what Ames has accomplished thus far, and for the direction their present work is taking, I've broken down their program into four discussion areas. This fourfold approach should allow you to project your specific situation into the Ames program and thereby make this intumescent session more meaningful. These areas are (1) the Ames contract program, (2) their military support program, (3) a market development, or technological utilization program, and finally (4) support for other agencies.

When designing coatings for applications in each of these areas (for example, a coating for a military support program as versus one for the Department of Transportation), one is always trading off such properties as quenching characteristics against such things as oxidative resistance and the actual temperature at which the coating intumesces. The point must be made that each individual application is unique in itself. You should have a feeling for this, after my brief comments in each of these four areas.

TABLE 1. THERMAL PROTECTION COATING  
FORMULATION NUMBER 45B3

	<u>Parts, wt</u>
Part A:	
Polysulfide polymer	14.1
Ammonium p-nitroaniline- o-sulfonate	47.0
Methyl ethyl ketone	28.9
Part B:	
Epoxy resin, liquid	14.1
Toluene	14.7
Part C:	
Tri(dimethylaminomethyl)phenol	2.8
Toluene	2.8

Contract Program. The contract program for intumescent coatings comprises at least three principal contractors.

The first of these represents a basic research contract with Dow Chemical at Walnut Creek. From this contract some 50 to 100 different kinds of polycyclic aromatic micro-substituted amines have been synthesized for Ames to evaluate as intumescent agents. As Dr. Parker mentioned, before evaluating these basic compounds, they must be converted from sodium to ammonium salts, and coupled to form sulfonamids. This type of information as it's gathered, and will continue to be gathered over the next several years, is fed by slightly different mechanisms into two other contractors. First of these is Avco. Avco never had a contract to study or to make intumescent coatings but have gotten into this business as a necessity of having this coating as a companion for foams (similar to the C47-type application we just saw in the movie). Avco was given seed capital (\$1 million) for a systems analysis and, as a consequence of this, organized a paint shop and thereby got into the business of producing intumescent coatings. Avco also applied to the Government for licenses to manufacture and sell the coating and they now enjoy a nonexclusive license in the United States and an exclusive foreign license. As perhaps the sole commercial producer of this intumescent coating in the world, Avco has implemented an aggressive market development program and advertising literature and samples are available from them. To date, most foreign interest has come from Japan and Germany. Japan has a very high level of consciousness of fire threat from earthquake as well as fires from multi-end collisions of automobiles and the like. They have conducted a number of significant fire tests which suggest that intumescent coatings would be useful.

It may be interesting to you to know just how many people have been and are still involved in the genesis of these coatings. The U.S. Navy set up a parallel program to that of Ames by independently securing intumescent agents from the Allied Chemical Corp. in New Jersey and at the same time empowered Thiokol to actually make sample quantities of paint for the Navy's own use. The expertise that Allied uses was based on laboratory work done at Ames under a National Research Council postdoctorate fellowship program conducted at Ames. The ammonium salts of the p-nitro aromatic amines of sulfonic acid were developed in this NRC program.

The Avco Corp. also has gotten the sodium salt from Allied and they've had it converted by two organizations, by Allied themselves and by Nianza, a small company nearby. Therefore, several organizations now have the capability of converting the sodium salt to the ammonium salt to make the final pigment that goes into this paint. Incidentally, Allied is now making the salt directly as an ammonium salt and this direct conversion process should result in a high purity product at reduced price. Again, to illustrate the competitive momentum which is being generated in the business community, the German chemical industry alleges to be able to provide these intumescent agents at about half the cost that Allied is now quoting.

Military Support Program. In addition to the two above-mentioned military applications, I'll touch on a few more in the hope that we might all benefit from some spin-off into one of your specific applications.

Before we leave the Mark 82 bombs, it should be noted that the basic requirement of that program was to apply no more than 100 mils of coating at a cost of no more than \$20 per bomb and get 5 min in the fire. Ames did get this with 40 mils of coating and got three times that length of time for cookoff. The present cost is somewhat in excess of \$20 per bomb, but, with full-scale production of the salt in this coating, cost could be reduced to \$8 per bomb. In addition to cost, the advantages of this coating are (1) good performance with cookoff, in terms of thermal protection, and (2) unlike any other that's been applied to weapon systems it has excellent high-temperature, high-humidity aging characteristics and good weathering characteristics.

In combination with foams, the coatings are also finding use on fuel tanks. Because of the excellent fuel resistance of the coating, these foam-coating combinations are being examined in jet fuel fighter tanks themselves. We should expect to see much wider use of foam/coatings combinations in the future.

The Air Force program has comprised two principal aircraft, the AX and the F-4. The F-4 fighter contains a lot of void or hell-hole areas which lend themselves well to the application of flexible foam with an intumescent agent in sacks, rods, or any form that can be easily inserted and then removed to inspect and repair and replace without activation.

I've already mentioned the use of the intumescent coating on the flexible foam in the tank itself. This is Ames's new contribution to the AX concept which is now being studied in the laboratory.

Figure 2 illustrates several of their present wide variety of interests. These coatings applications range from military (structural frames for the A4 fighter, Mark 82 bombs, and rocket launchers) to civil considerations (air cleaner/carburetor complex of the Pinto automobile, and the engine housing compartment of a cabin cruiser line produced by Auto Coast Boat).

Hughes Aircraft, the other large contractor, has been awarded two contracts. Their first contract was directed toward understanding intumescent agents on the intumescent efficiency of the system in terms of thermal protection. As a result of this contract, there are now some general rules for the optimization of degree of fire protection that can be obtained from these coatings as based upon the glass temperature of the polymer, the swelling volume of the polymer, the cross-link density of the polymer, and the percent of intumescent agent.

For the second contract, Hughes entered into a funding agreement with the Furane Paint Co. and this program was designed to (1) develop scale-up techniques for production quantities of paint, and (2) supply Ames with the quantity needed for their research. A major contribution was made by shortening the curing time from 10 to 2 days. This is especially important to the Navy because the extended cure time had not lent itself to the nominal production line cycle for bombs. Protection against weapons cookoff is so important to the Navy that they were continuing with the Mark 82 program in spite of this problem. The accelerated cure has now overcome this with no compromise in coating performance.

The flexible or "wrap-around" formulation is also an outgrowth of this Hughes study and it was basically accomplished by increasing the polysulfide resin component in the basic 45B3 coating formulation.

Another extremely interesting military application is the development of new types of caseless ammunition. This uses the same intumescent chemistry but takes it the other way around to obtain a system which might intumesce at a low heating rate, but, when appropriately boosted with the right kind of explosive, could burn cleanly, since we're dealing with a nitro-substituted aromatic compound which is able to polymerize to give a ladder structure. We can expand on this concept to include multinitro substitution of the aromatic system and possibly achieve this condition. The idea of building a safe, caseless ammunition which would stand a fire but would boost its way into clean gun burn, say a 30-millimeter cannon, is an X15 concept that Ames would like to get into the laboratory.

Market Development Program. Since each of my four arbitrary discussion areas are somewhat market development-oriented, I'll delve right into one of the largest commercial application areas--the building industry. As soon as we talk building materials, it is necessary to consider economics and, of course, economics are always a problem. You can't get the properties you want at a cost which is commensurate with what the building materials trade will bear. In other words, to get the kind of chemistry going for you that you basically need is an expensive proposition. Along with cost, there are some extremely difficult processing problems. We're dealing with polymers which are so far above their heat distortion point during much of the processing that even powder metallurgical techniques and so-called hydrostatic forming and isostatic forming/processing are the order of the day.



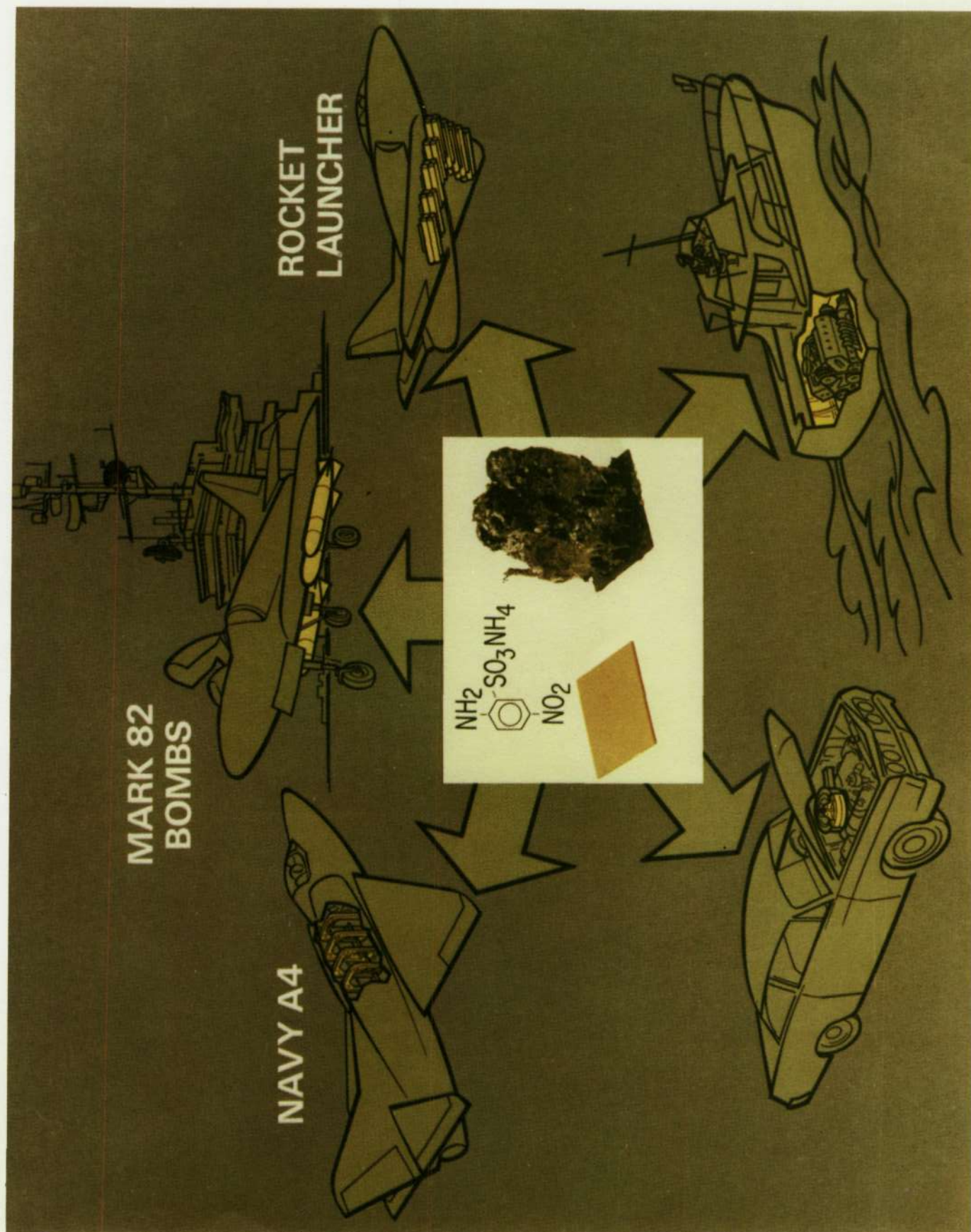


FIGURE 2. EXAMPLES OF APPLICATIONS FOR LUMINESCENT COATINGS



Even with these problems in mind, we can recognize a legitimate technological breakthrough with the intumescent coatings using the nitro substituted aromatic amines. The cost of \$1-3 per pound has been reduced by a factor of 10. Certainly this doesn't compete with casein or starch materials, as used for indoor building applications. They are not meant to. Along with this price break we have not obtained processibility which heretofore was not available by polymerizing in situ. Of importance here is the fact that this combination of reduced cost and processibility should now make these coatings attractive to the building industry. However, there are other problems which are specific to intended use applications. Certainly it is pertinent in a discussion of this type to comment on two of the most serious of these problems--toxicity and oxidative stability. When discussing toxicity, it should be noted that these coatings are effective because they transpire. And they transpire by polymerizing to give off small molecules of water and  $\text{SO}_2$ . We know that  $\text{SO}_2$  is toxic, not severely toxic when one compares it with HCN or HF, or some of the results of the pyrolysis of Teflon. Also, with all of these intumescent systems, one is continually trading quenching efficiency against the intrusion of CO, which is going to do its own killing in its own way.

All of these intumescent materials, without exception, must not be applied indiscriminately. If we put the fire-retardant coating in the room on the furniture and introduce toxic gases, we're in trouble; these materials must be relegated to areas which are remote from habitable parts of a building.

Second only to the problem of toxicity is that of oxidative stability. Previously, we have been discussing the short-term fire such as an aircraft fire of 12-15 minutes, possibly 30 minutes at the most. But if your requirement is an hour immersion in a fire, you're going to have to have improved oxidative stability of the char (the black coating system which arises when you intumesce this material). The coatings now in hand have been designed for application in a JP4 fuel fire-type environment as you saw in the movie. They are not particularly well suited for severe oxidizing environments where one has a very highly oxidizing flame. And the reason for this is simply that various tradeoffs have been made in processing, in chemistry, and fire protection and the like. Ames possesses the expertise to formulate for this long-term fire and they should be prodded by you into doing so. In the meantime, oxidative stability is a problem which must be reckoned with.

When you consider your particular application (for example, in the building trade), you should classify it according to the cost, processibility, application technology techniques, and finally the whole broad question as how does fire enter into, how does toxicity enter into the fire question. As a cast in point, APT Associates, who is a TU contractor, attempted to do this for the insulation and fire protection of the steel structure of high-rise buildings. And here's a situation where the localization of the coating and its function to prevent buckling of the building is remote from the habitable part of the building. The point here is that there is a keen interest in using these materials in the support structure of buildings. In the past, intumescent coatings have lacked adhesion and simply dropped off. With the advent of the chopped fiber coating, this type of problem should also be solved.

Protecting steel beams from buckling in temperatures up to 1000 degrees is now possible. Proper application and inspection are equally important. The inspections should not only cover the initial application (which is critical) but should insure that workers and all others who follow do not chip off or rip away the protective coating. Consider an apartment building where one is protecting against the spread of fire from one unit to another and you fail only because someone knocked off your coating simply to hang a piece of wallboard or install some plumbing.

The same idea of a fire break applies to more expensive individual houses to protect against fire radiation as well as from the fire itself. Pursuing this further, it is highly desirable to have protection of housing against flying branches in a brush or forest fire. Right now with shingle roofs we're getting fire jump 2, 3, and 4 miles in a brush fire.

You might ask why we just don't continue along the path of least resistance and build better passive systems. For example, simply use more gypsum board, foam, glass, or anything to stay inert in regard to ignition--and this is exactly what the building industry has been successfully doing for years, in spite of its vast knowledge in organics. A good example here is that of Upsom board (Figure 3). The Upsom Company includes this picture in its advertising to correctly show the good fire retardance of its product. Although the board is considerably charred, the 2 x 4 underneath has been effectively shielded. The question then arises "Should we stay mineral? Should we stay passive?"

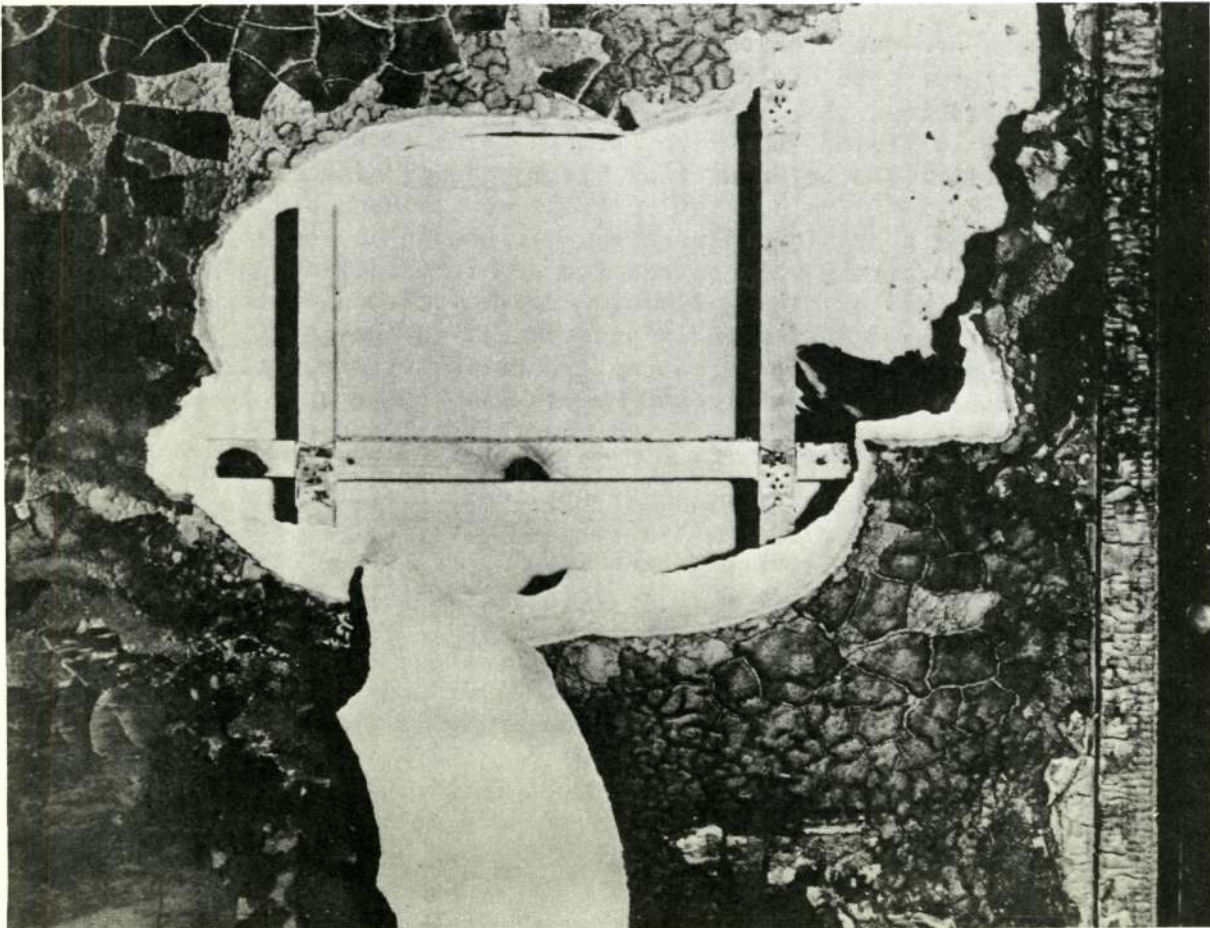


FIGURE 3. REMOVAL OF BURNED WALL REVEALS INTACT CONDITION OF UPSOM BOARD AND DEMONSTRATES ITS EXCELLENT FIRE RESISTANCE

We believe that the answer is "no" for the following reasons. Already HUD is asking for assistance in the mass producibility of housing and in a very short time this need will become chronic. In the meanwhile, the building materials trade has been stymied by an apparent insurmountable problem in processibility (for example, casting concrete buildings, casting combinations of concrete and gypsum, and this kind of system). Therefore, if concrete is not receptive to the mass production techniques we're talking about, we must turn to organics. We may be more advanced in this organic technology than is commonly believed, because there appears to be somewhat of a zeitgeist phenomenon unfolding. Companies (for example, Dow Chemical) have enormous amounts of chemical R&D locked in closets because they were not economically "right" for the market. Now, in light of improved economics (from mass production) and public pressure, when one says "quenching agents for polystyrene or polypropylene" several million dollars and years of research will tumble out.

To summarize the present relationship of intumescent coatings to the building trades, one would have to say it is a situation of enormous, almost unlimited, potential. Still, it will require an equally enormous amount of dollars and effort in terms of design, modification, and tailoring to realize this potential. This uncovers a basic fact of technological transfer that has been said many times today - NASA technology must be modified if it is to be used, as there is little direct overlapping between aerospace and the domestic markets. Both dollars and effort are required to capitalize on this knowledge.

Another TU application, and this is a new activity for Ames, is that of the American Railroad Association. The basic requirement here is to coat tank cars with the intumescent paint in an effort to obtain 3-45 minutes' protection, especially for cars carrying liquid hydrocarbons. This application has presumably been solved with the long fiber version of the Ames intumescent coating. What is significant here is, this knowledge will bounce right back to the building industry for protecting high-rise building structures.

The ARA's problems and their solution also suggests application of the long fiber intumescent paint to protect very large tankers. We all know that there is a very short supply of methane in Europe and the idea of building very massive tankers to permit the transport of these petrochemical gases to Europe is in the works. A past situation which arose with Owens-Corning is of interest for still another reason. Owens-Corning is manufacturing fiber glass polyester styrene resin shower stalls. However, with one out of every two installations, the plumbers would set them on fire with a brazing torch when fitting pipes. Ames found that a very thin coating, about 3 or 4 mils, of 45D3 (without any fibers in it) would prevent the torch off with the butane plumber's torch. Owens-Corning then approached Avco and was essentially turned down because of the small volume of material required. Owens then set up a paint shop of their own and are now successfully making and applying the material by themselves. Here's a situation where the market itself has generated a new user.

Before we leave the area of Market Development, it would be well to mention the National Bureau of Standards and the present situation with polypropylene carpet. About one-half of the polypropylene carpet that is used in our country today is manufactured here in the United States, yet none of this 50 percent will pass the Bureau's specifications. This suggests the need for

an advanced intumescent agent for use as a back coating which would activate when in contact with an ignition situation. This brings up the question of what specifications are we required to meet today in 1971.

As you know, the specification bible for intumescence is still the comprehensive U.S. Fire and Safety Act of 1968. Mainly as a result of this prodding, more specific specifications have been written, such as

- (1) Federal Specification TT-P-0026B
- (2) ASTM - E 84-67
- (3) Underwriters Laboratories -UL 723  
(25-foot tunnel test)
- (4) Federal Test Method 6142  
(serviceability requirement)
- (5) NFPA -255

You should be aware of these if only because they represent today's minimum acceptable performance base line.

Support for Other Agencies. My final discussion area is concerned with NASA-Ames support for other agencies. The objective of my comments here is unchanged; that is, I would like to stimulate your thinking to the point where your particular need meshes with what can or might be supplied by NASA intumescent technology. Many agencies should be mentioned here, certainly HUD, FAA, and DOT.

In approaching HUD, we've already alluded to the change in philosophy which is required from typical Ames applications. For example, with a space-craft or airplane we want to prevent the fire from occurring in the first place. HUD applications require a lower rate of protection since they are primarily concerned with time delay to remove people from the fire. Also, mass producibility will require a radically different price structure from that supported by aerospace.

Closely allied to HUD interests are other agencies such as HEW; (for example, hospitals and nursing homes are covered by the Health Service and Mental Health Administration of HUD and the Medicaid-funded areas are covered by the Social Security Administration of HUD). Another hospital and nursing home watchdog is the Veterans Administration, who has now accepted the codes of the National Fire Protection Association. Still another agency is the Department of Commerce who closely checks the market in mattresses. Their current (proposed) standards were recently published in the Federal Register on September 9, 1971.

Interest is mushrooming and two facts can not be denied. First, pressure is being exerted to apply this intumescent technology to domestics now, not tomorrow, and second, the business community is actively responding to this challenge. Typical of this is the Chemical and Engineering News article of October 18, 1971, about flame retardants which suggests that this market may quadruple by 1975, in only 3 years.

The Department of Transportation is a fertile area for this new technology because of their concern in preventing fires from rear-end collisions in automobiles. The use of foam/coating combinations is ideal for engine compartments because there is no problem of toxicity. Ames personnel have



worked with Volkswagen to use the intumescent combinations in a dual function to act as both a fire barrier and as a noise dampener. Earlier I mentioned Japanese concern for this problem and this was justified by the results of a test in which they lined Datsuns and Toyotas in the street and then started a fire by involving one or two gas tanks. Fire jump occurred every 17 seconds right down the freeway. Obviously there is a solution to this problem somewhere with the foam/coating combinations.

The FAA is completely involved with their own testing program; however, a new application has just arisen in which Ames will participate. This involves the use of intumescent materials as fire curtains to be used in aircraft as a second line of defense following fuselage rupture. This test will be conducted with a DC7 and it is still about a year and one-half away.

Summary and Conclusions. Before closing, I'd like to briefly summarize all of this and offer several conclusions. In general, it should be reemphasized that there is no mechanism today for correcting the deficiencies in products which have been developed for other applications. There have been attempts made to use the intumescent coatings simply by direct substitution for existing materials. Results have never approached optimum because they are not directly substitutable, either on a cost or a pound-for-pound basis.

To correctly apply the intumescent principle to any specific situation, we should be aware of a mystique which recognizes that, for every type of fire and ignition, there are special kinds of shapes and geometries, of pre-radiating surfaces--almost a personality to a particular fire in a particular situation. As a consequence, we must construct a fire scenario to assist in determining the best protection while minimizing the overall hazard.

The future undoubtedly will bring wider and more refined application of the intumescent principle. However, there are many other ways to construct materials to deal with the problem of quenching, of extinguishing, of smoldering, and even toxicity. For example, Ames has developed a set of micro-encapsulants which are released thermally and provide a momentary deluge of a quenching agent. However, if you miss it with the surface, then you're in trouble. It does prevent ignition, so this is one alternative to intumescence.

Because people and intumescence are incompatible, there is a need to develop an improved coating system with high temperature resistance that would form a char but would also be nonburning, nonsmoking, and nontoxic. Polymers which could be made thermally and in place might fill this need. Illustrative of these are the types Dr. Dunnivant mentioned earlier, for example, the polybenzimidazoles. Studies of this type are continuing at Ames.

For the majority of today's fire protection applications, the technology is now in hand--and--in summary--the ammonium salt of p-nitroaniline sulfonic acid makes this possible because of these advantages -

- (1) It provides excellent thermal protection (that is, good performance with cookoff).
- (2) It possesses superior aging characteristics.
- (3) It possesses superior weathering characteristics.
- (4) It provides excellent resistance to high temperature.
- (5) Similar resistance to high humidity.

Numbers 3, 4, and 5 are possible because the salt is hydro-litically stable and is easily sealed in the resinous binder.

- (6) It has excellent adhesion and toughness, or durability.
- (7) Its availability spans many forms, from the basic 45B3 coating to the agent itself suspended in a sack. Perhaps future use may show that the greatest advantage of this availability is its ready compatibility with foams for use in foam/coating combinations.
- (8) It is economically attractive. Although this is a relative consideration, it must be mentioned again because of the significant break in the price structure and the processibility of the salt.

These eight basic advantages can be successfully applied to almost any end-use situation. And I should stress the point that Ames, Avco, and Battelle personnel are available for further, more detailed, discussion as would be appropriate to your particular situation.